CATALYTIC CONVERSION OF C_5 OLEFINS TO PROPYLENE BY METATHESIS REACTIONS

BY

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A Thesis Presented to the

DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the

Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

DECEMBER 2016

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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2016

Dedicated to my parents who gave me support in my live,

to my sisters, friends and all people love and care about me.

ACKNOWLEDGEMENTS

All praise is to Allah the lord of the worlds. And may the peace and blessings of Allah be upon the Holy Prophet Muhammad, the leader of mankind.

I would first like to extend the warmest appreciation to my supervisor, Dr. Sulaiman Al-Khattaf, for his mentorship, valued guidance and critical supervision throughout the planning, execution, and communication of my thesis work. I am extremely thankful for the time devoted by supervisor to critically review and constructively criticize my written materials.

My sincere thanks also go to Dr. Muhammad Naseem Akhtar for his countless efforts, assistance, professional advices, his long discussions that helped me to build the chemistry background related to my research and his patience in reading and commenting on many revisions of this work. My appreciation also goes to my other thesis committee members; Dr. Mohammed Ba-Shammakh, Dr. Nadhir A. Al-Baghli and Dr. Isam Al-Jundi for their immense assistance throughout this work.

My parents and sisters, I am deeply appreciative for their patience, encouragement and love throughout the study. I also want to offer my regards and appreciation to my friends, colleagues and all of those who supported me during the completion of the thesis work.

I would like to acknowledge the support provided by the National Plan for Science, Technology and Innovation (MAARIFAH) under (King Abdulaziz City for Science and Technology). The support from Chemical Engineering Department (CHE) and Center for Refining and Petrochemicals (CRP) of KFUPM is highly appreciated. Also I want to thank the Ministry of Higher Education, Saudi Arabia to give me this opportunity to peruse my graduate studies.

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LIST OF ABBREVIATIONS

FCC	:	Fluid Catalytic Cracking
MTO	:	Methanol to Olefins
LPG	:	Liquefied Petroleum Gas
PDH	:	Propane Dehydrogenation
LNG	:	Liquefied Natural Gas
MTP	:	Methanol to Propylene
VGO	:	Vacuum Gasoil
DCC	:	Deep Catalytic Cracking
HF-FCC	:	High Severity Fluid Catalytic Cracking
UOP	:	Universal Oil Products
OCT	:	Olefins Conversion Technology
FBCC	:	Fixed Bed Catalytic Cracking
MOI	:	Mobil's Olefin Interconversion
WWFC	:	World Wide Fuel Charter
MCM	:	Mobil Composition of Matter
SBA	:	Santa Barbara Amorphous

MMS	:	Mesoporous Molecular Sieves
OMA	:	Organized Mesoporous Alumina
HMS	:	Hexagonal Mesoporous Silica
IUPAC	:	International Union of Pure and Applied Chemistry
MWW	:	MCM-22 (Mobil Composition of Matter-22)
MFI	:	ZSM-5 (Zeolite Socony Mobile-5)
CTABr	:	Cetyltrimethylammonium Bromide
PID	:	Proportional –Integral-Derivative
WHSV	:	Weight Hourly Space Velocity
GHSV	:	Gas Hourly Space Velocity
GC	:	Gas Chromatographic
FID	:	Flame Ionized Detector
TEOS	:	Tetraethoxysilane
HMI	:	Hexamethyleneimine
RPM	:	Round Per Minute
TOS	:	Time On Stream
XRD	:	X-ray Diffraction
BET	:	Brunauer-Emmett-Teller

$\mathbf{S_{BET}}$	:	Surface Area Brunauer-Emmett-Teller
$\mathbf{V_{tot}}$	:	Total Volume
ICP-OES	:	inductively coupled plasma-optical emission spectrometry
ACAC	:	Acetyl acetonate
Ru	:	Ruthenium
Re	:	Rhenium
Mo	:	Molybdenum
W	:	Tungsten

ABSTRACT

Full Name : Mohamed Ali Mohamed Ali Ibrahim

Thesis Title : Catalytic Conversion of C_5 Olefins to Propylene by Metathesis Reactions

Degree : Master of Science

Major Field : Chemical Engineering

Date of Degree : December 2016

C_5 olefins produced as a by-product from steam crackers and FCC units have low value as gasoline blending stock. However, low value C_5 olefins can be converted to valuable product such as propylene by metathesis reaction. A series of catalyst were prepared based on metal (molybdenum and tungsten) oxide supported on conventional silica (SiO_2), mesoporous material (MCM-41 and SBA-15) and microporous material (MCM-22). Catalysts were prepared following two methods i.e. thermal spreading and wet impregnation. In case of thermal spreading method, the support was mixed with metal oxide by grinding, whereas wet impregnation method was obtained by suspension of support in aqueous solution of metals.

Catalysts were characterized using X-ray powder diffraction (XRD), N_2 adsorption/desorption isotherms and ICP-OES. XRD and N_2 adsorption-desorption study revealed that the architecture and mesoporous character of supports were preserved in catalysts while ICP-OES used to determine catalyst metal loading.

Also prepared catalysts (6 wt. % of metal) were investigated in the transformation of 2-pentene in a flow fixed-bed reactor at different reaction temperatures. The MoO_3

catalysts based on conventional silica exhibited the lowest activity (8%) and mostly isomerization of 2-$C_5^=$ proceeded. MoO_3 on MCM-22 exhibited the highest conversions (79%) but catalyzed isomerization and cracking of 2-$C_5^=$ as major reactions. MoO_3 and WO_3 catalysts supported on mesoporous MCM-41 and SBA-15 showed metathesis reaction of 2-$C_5^=$ resulting in the formation of propylene, C_4 olefins and $C_{6+}^=$ (hexenes and higher olefins) as major products. The results revealed that catalysts based on MCM-41 exhibited higher activity and stability as compared to that of SBA-15. The 2-pentene conversion increased in the following order of catalysts used MoO_3 /SBA-15 < $MoO_2(acac)_2$ /SBA-15 < $MoO_2(acac)_2$ /MCM-41 < WO_3 /SBA-15 < WO_3 /MCM-41.

Addition of ethylene to the 2-$C_5^=$ feed with 2-$C_5^=$: $C_2^=$ molar ratio (1:1) increased selectivity to propylene due to cross metathesis of ethylene with 2-pentene to produce propylene and 1-butene whereas production of C_6^+ olefins were substantially limited.

ملخص الرسالة

الاسم الكامل : محمد علي محمد علي ابراهيم

عنوان الرسالة : التحويل الحفزي لاوليفينات ال C_5 الي بروبيلين عن طريق تفاعلات الاحلال و الابدال

الدرجة : درجة الماجستير

التخصص : هندسة كيميائية

تاريخ الدرجة العلمية : ديسمبر 2016

تنتج اوليفينات ال C_5 كمركبات ثانوية من وحدتي التكسير الحفزي و التكسير بواسطه البخار و تكون ذات قيمة منخفضة عند اضافتها لخليط الوقود. يمكن تحويل هذه القيمة المنخفضة الي مركبات ذات قيمة عالية كالبروبيلين باستخدام تفاعلات الاحلال و الابدال. حيث تم تحضير مجموعه من المواد الحفازة المبنية علي اكاسيد عنصري التنجستن و الموليبدنيوم المثبتة علي السيليكا العادية (SiO_2) و المواد المسامية (MCM-41 و SBA-15) والمواد متناهية الصغر (MCM-22) وفق طريقتين للتحضير هما الانتشار الحراري و التلقيح المبلل. في حالة الانتشار الحراري يتم خلط المواد المدعمة المحمصة مع اكاسيد المعادن عن طريق الطحن، اما في حالة التلقيح المبلل يتم خلط محلول المواد المدعمة مع محلول اكسيد المعدن المطلوب.

لقد تم فحص خصائص المواد الحفازة المصنعة و ذلك باستخدام جهاز انكسار الاشعة السينية (XRD) ، و امتصاص وطرح النتروجين (N_2 Isotherm) و جهاز ICP-OES. جهازي ال XRD و N_2 isotherm لاثبات ان الخصائص المسامية و البنية الاساسية التي تتمتع بها المواد المدعمة قد تمت المحافظة عليها عند تحضير العامل الحفاز ، اما جهاز ICP-OES لحساب كمية المعدن المضافة للمواد المدعمة.

ايضا تم اختبار فعالية جميع المواد الحفازة المنتجة (نسبة المعدن 6%) في تحويل 2-بنتين باستخدام مفاعل انبوبي ثابت الحشوة عند درجات حرارة مختلفة. اظهر الحفاز MoO_3/SiO_2 نسبة تحويلية بسيطة من المواد الخام قدرت بي 8% و معظمها تفاعلات ازمرة ل 2-بنتين ، بينما اعلي نسبة تحويلية قدرت ب 79% بواسطة الحفاز MoO_3/MCM-22 و معظمها تفاعلات تكسير و ازمرة كتفاعلات اساسية. اما المواد الحفازه المبنية

علي MoO_3 و WO_3 المثبتة علي المواد المسامية قد اظهرت جميعها تفاعلات الاحلال و الابدال كتفاعلات اساسية لانتاج البروبيلين و اوليفينات ال C_4 و C_6^+ كمركبات اساسية. اثبتت النتائج ان المواد الحفازة المثبتة علي MCM-41 ذات كفاءة عالية و فعالية اكبر من تلك المثبتة علي SBA-15 . و ان النسبة التحويلية للمادة الخام تزيد باستخدام العوامل الحفازة المنتجة وفق الترتيب التالي

MoO_3/SBA-15 < $MoO_2(acac)_2$/SBA-15 < $MoO_2(acac)_2$/MCM-41 < WO_3/SBA-15 < WO_3/MCM-41.

اضافة الايثيلين كمادة خام مع ال 2-بنتين وفق النسبة المولية ايثلين:2-بنتين (1:1) ادي الي زيادة انتاج البروبلين نتيجة لي تغيير التفاعل من احلال و ابدال ذاتي الي متقاطع مما ادي ايضا لزيادة انتاج ال 1-بيوتين و خفض انتاج ال C_6^+ .

CHAPTER 1

INTRODUCTION

1.1 Background

C_5 olefins mainly consist of five isomers such as 1-Pentene, 2-Pentene, 2-Methyl-1-butene, 2-Methyl-2-butene and 3-Methyl-1-butene. Figure 1.1 shows the structure of different isomers of C_5 olefins [3, 8].

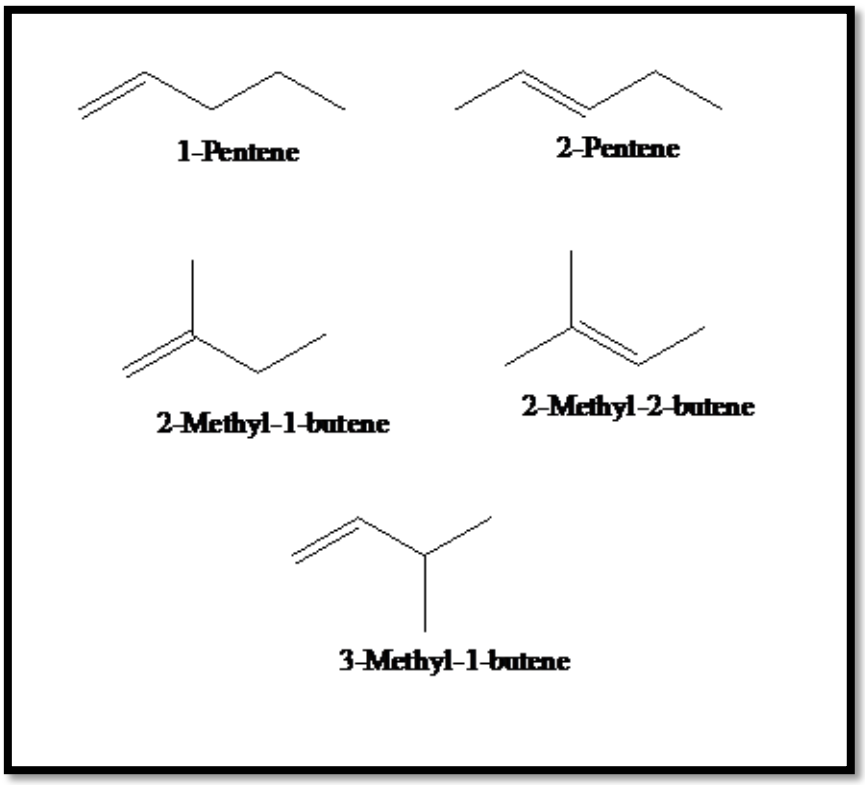


Figure (1.1): Isomers of C_5 olefins

C_5 hydrocarbons are produced mainly as a by-product from naphtha steam cracking and also refinery fluid catalytic cracking unit (FCC).Table 1.1 shows the typical composition of C_5 raffinate that produced from FCC unit [3,8].

Table (1.1): Composition of C_5 raffinate that produced from FCC unit

Component Name	Weight %
Pentane	33.4
2-Methyl-2-butane	25
1-Pentene	8.3
2-Methyl-2-butane	25
Cyclopentane	8.3

C_5 hydrocarbons streams have little value as gasoline blending stock due to their high volatility. Low value C_5 olefins can be converted to more valuable products (mainly propylene) via cracking or Metathesis and can be integrated with a fluid catalytic cracking (FCC) unit or a naphtha steam cracker or methanol to olefins (MTO) unit.

Propylene is one of the most significant basic chemicals "building block" used in petrochemical industry. It is also used as feedstock for a wide range of chemical products and polymers like polypropylene (PP), cumene (isopropyl benzene), acrylonitrile, propylene oxide (PO), oxo-alchohols, isopropyl alcohol, acrylic acid and other chemical intermediates. The world propylene demand increased from 37.2 million tons to 67 million tons for the period 1995 and 2006. Global Demand for propylene was increased by 5-6% annually for the period of 2007-2015 and raised up

to 100 million tons by 2016 [1]. The future demand between 2017 and 2025 is expected to increase by 3% which indicates that the demand will rise to 132 million tons in 2025 [1-3, 5].

The main reason for increase in the demand for propylene is the high consumption of polypropylene. Figure 1.2 below shows how propylene demand increased due to high consumption of polypropylene for the year 2013 [4].

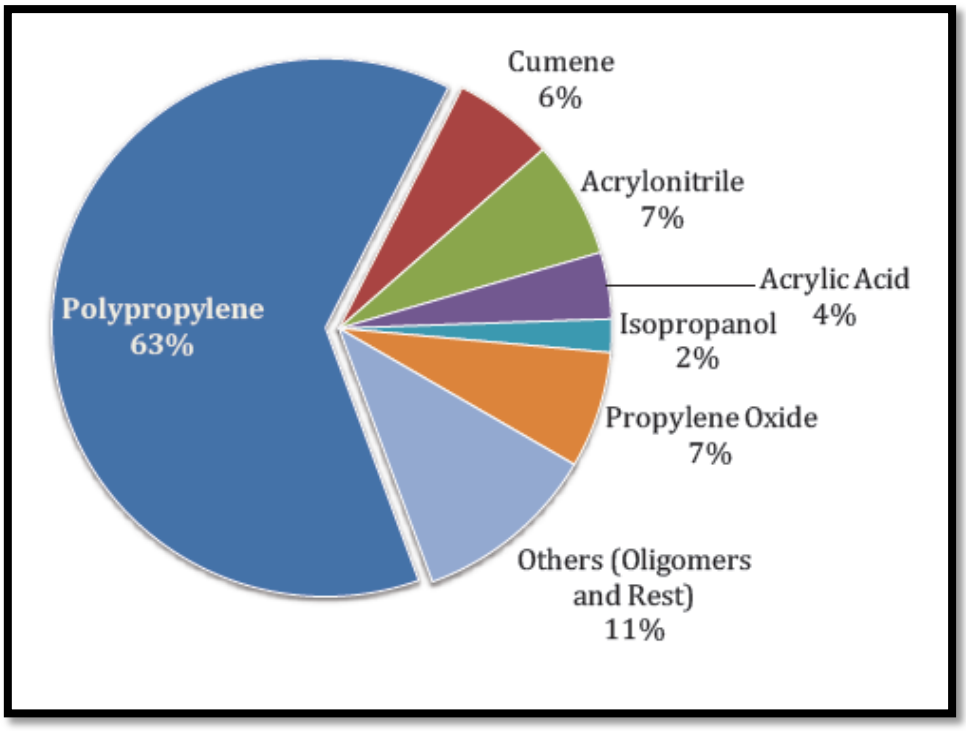


Figure (1.2): Global consumption of propylene derivatives [4]

Propylene derivatives are generally converted to a wide range of end-use applications such as automotive sector, automobiles and thermo plastics, construction, clothes, packaging, paints, inks and electronics [2]. Figure 1.3 shows overall propylene

derivative and their final application starting from the raw material (crude oil) then refinery and petrochemical industries.

Main propylene derivative is polypropylene. It is one of the most versatile of the bulk polymers due to mixing of good mechanical and chemical properties. Polypropylene is used to produce mechanical parts, fibers, electronic and electrical appliances, containers, automobiles plastics, woven bag, bottle caps, toys, food storage, kitchen tools, carpet, and furniture [8].

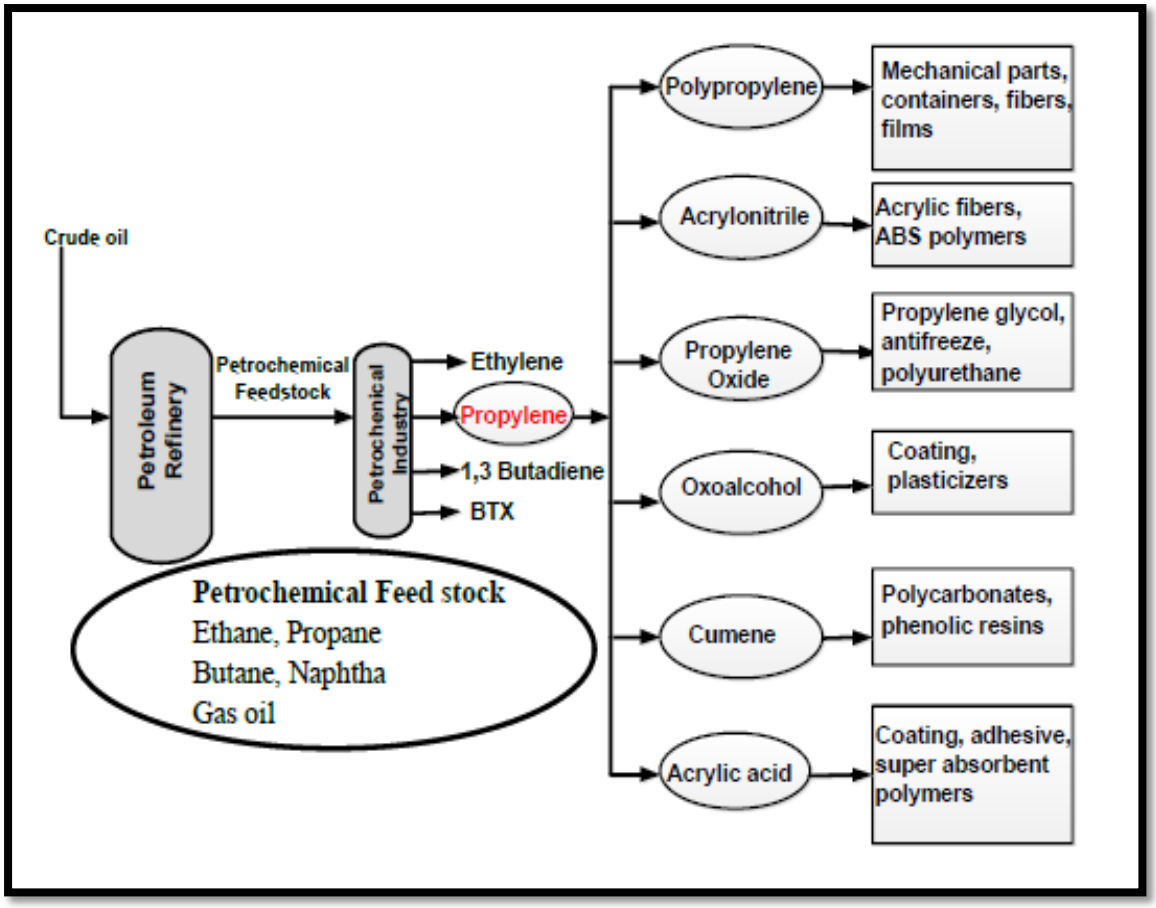


Figure (1.3): Conversion of crude oil to propylene derivatives and their uses [8]

Current global production of propylene is over 90 million tons per year. Propylene is produced commercially by several technologies; but the main two processes are steam cracker (ethylene) and fluid catalytic cracking (FCC) [3, 5].

In most of the steam cracking units, there is a typical ratio (1:0.65) for ethylene-propylene production depending on the feedstock [1, 3]. So the quantity of propylene produced from steam cracker has become fixed. FCC units are mainly used to produce gasoline with very high yield and propylene is produced as a by-product of gasoline with low quantities which are not enough for the high global consumption. Increasing the propylene yield is not economically feasible due to the importance of gasoline [7].

Nevertheless, to fill the gap between the supply and demand of propylene, refineries have introduced some new technologies and modified catalysts to capture more propylene from fluid catalytic crackers (FCC) but this solution can only increase the propylene yield by 5 wt% [1].

Therefore, other alternative processes were developed for propylene production such as propane dehydrogenation (PDH), olefins catalytic cracking (C_4 to C_8) [7], metathesis [11] and methanol to olefin (MTO) [8]. In contrast, with the increasing technologies of petroleum refining, large quantities of C_5 are produced.

In the effluents from a steam cracking units, the C_4 output is 30-40% of the ethylene yield and contain > 90% of alkenes and dienes. In FCC units, C_4 output is 10-13% of the feeds and contain > 50% of alkenes, as shown in Table 1.1 [7]. From Fisher-Tropsch syntheses, a large amount of low value C_4 olefins are produced [3].

In order to fulfill the high demand of propylene, low value C_5 resources from the steam cracker and FCC units should be upgraded and converted to high valuable propylene product and this is one of the main objectives of this thesis.

1.2 Technologies for Propylene Production

Technologies for propylene production can be divided into three main categories:

1) Conventional technologies

2) On-purpose technologies

3) Bio-propylene.

More than 88% of propylene is produced commercially from conventional technologies specially from steam cracking unit as a by-product of ethylene and fluidized catalytic cracking (FCC) as a by-product of gasoline. Several alternative processes are also used for propylene production such as propane dehydrogenation (PDH), high severity FCC, olefins catalytic cracking (C_4 to C_8), metathesis, methanol to olefin (MTO) and bio-propylene technologies. [8]

Main technologies being used for production of propylene are summarized in figure (1.4) where as production of propylene from various feed streams and technologies are summarized in figure (1.5). [6]

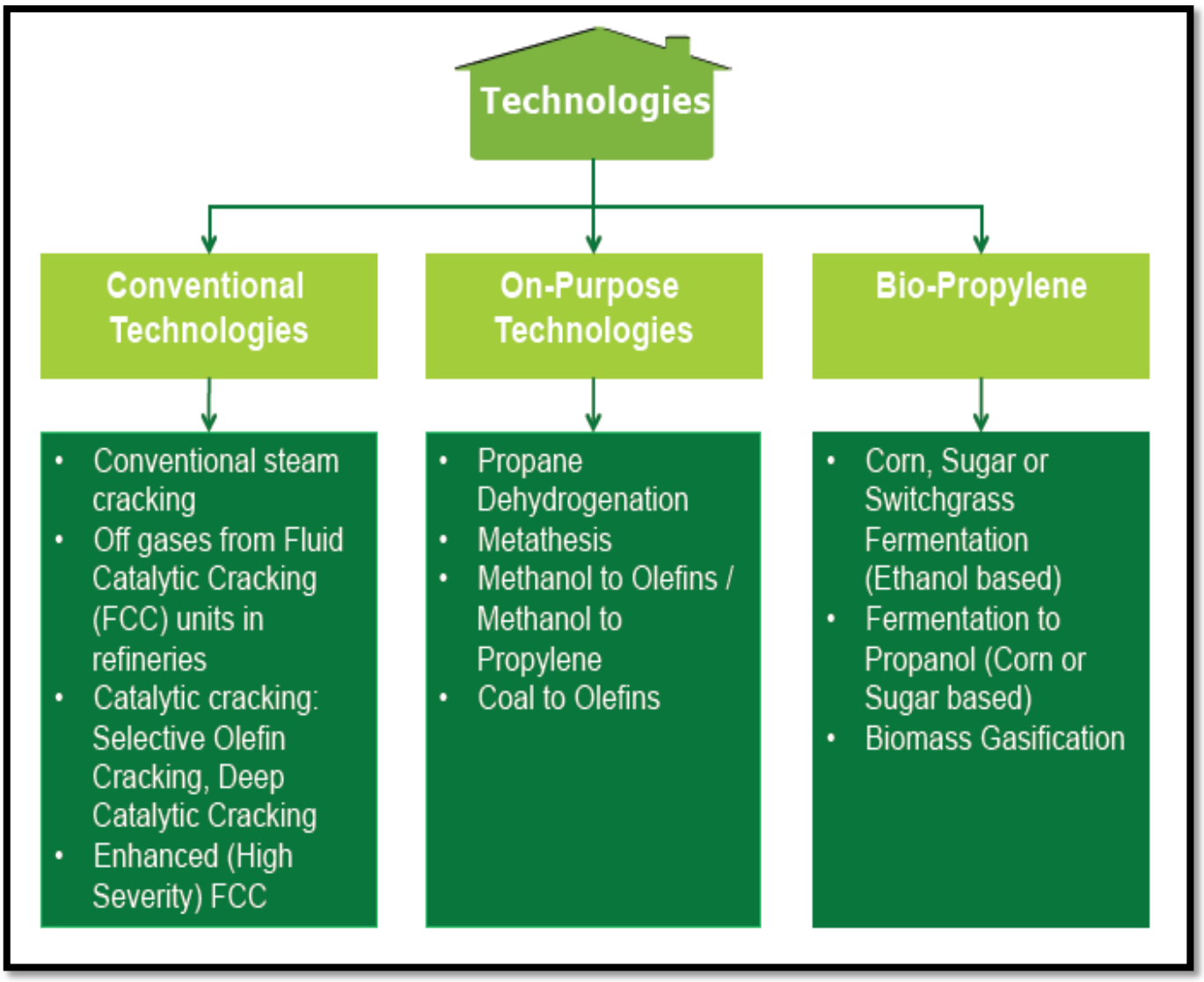


Figure (1.4): Main technologies for propylene production [6]

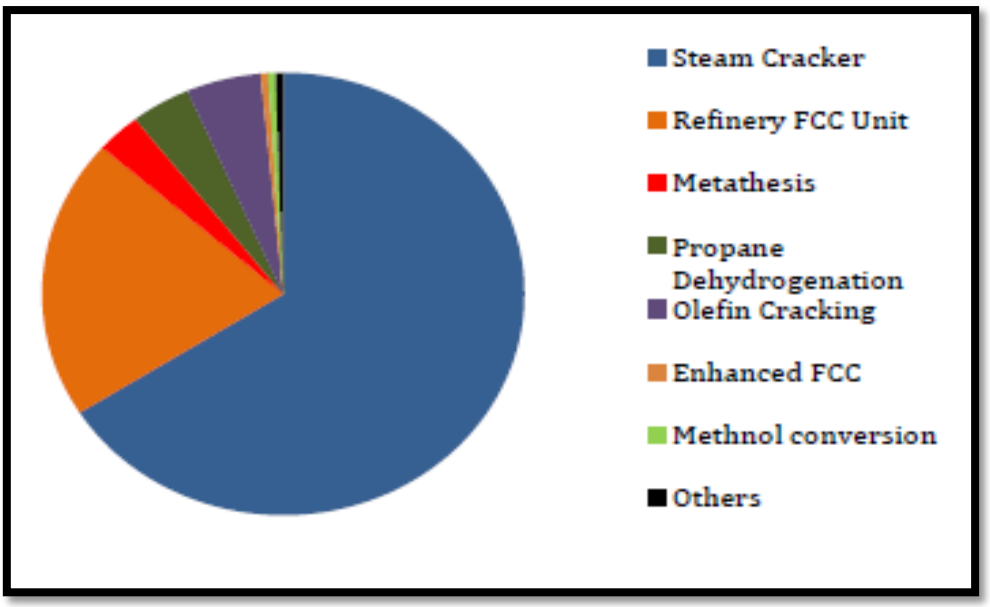


Figure (1.5): Propylene production from various feed streams and technologies [6]

1.2.1 Steam Cracking

Steam cracking unit is considered as a heart of petrochemical complex, it produces the main building blocks for petrochemical industry like ethylene, propylene, butadiene, aromatics, and acetylene. This technology was developed over 60 years ago. Current global production of ethylene is almost 112 million tons per year from steam crackers and the total amount of the propylene produced from these steam crackers as co-product is about 36 million tons per year. Feedstocks usually consist of many hydrocarbons like ethane, liquefied natural gas (LNG), liquefied petroleum gas (LPG), naphtha and gas oils. The distribution of co-product depends on main two variables: feedstock type and operation severity [2, 3, 9].

Steam cracking reactions are fundamentally bond cracking so they require very high energy leading to olefin production. The favorable operating conditions are high temperature (because the reaction is highly endothermic) and lower pressures. For

gaseous feed like ethane the temperature range from 750 to 800ºC, pressure range from 1 to 1.2 atm and steam /ethane ratio is 0.5. For liquid feed like naphtha the temperature is around 800ºC, pressure 1 atm and ratio of steam /hydrocarbon in the range from 0.6 to 0.8. The main product of the steam cracking is ethylene, and propylene is produced as a primary co-product of ethylene. Feedstock is sent to steam cracking furnace at a high temperature from 750 to 800ºC depending on the feedstock type, the molecules bonds break in the presence of steam. Hydrocarbons partial pressure is decreased by using steam which also reduces carbon deposits. Then, the cracked gases are cooled and sent to demethanizer to separate methane and hydrogen and after that, gases are treated in order to remove effluents. Thereafter, gases moved to the fractionators to separate ethylene. The fractionator bottom outlet is sent to the separator to split up ethane and C_3^+ products. Liquid feedstocks produce more products such as benzene, xylene, toluene that can be used in petrochemical industries. From ethane steam cracker, ethylene yield is 76% while propylene yield is 3%. In contrast, from liquid feedstocks like naphtha steam cracker, propylene yield is increased up to 16% while ethylene decreased down to 31% [3, 6].

The demand for ethylene is higher than propylene, and to an extent the yield of propylene can be increased depending on the type of feedstock, therefore it won't be possible to cover the increasing consumption of propylene from the steam cracker [3].

Table (1.2): The products yield from different feedstocks in a typical steam cracker [3]

Yield of products (wt%)	Feedstock				
	Liquid feedstocks		Gaseous feedstock		
	Naphtha	Gas-oil	C_3H_8	C_4	C_2H_6
$H_2 – CH_4$	26	23	28	24	13
Ethylene	30	25	45	37	80
Propylene	14.1	14.4	14.0	16.4	1.11
Butadiene	4.5	5	2	2	1.4
Mixed butenes	8	6	1	6.4	1.6
C_5^+	18.5	32	9	12.6	1.6
Propylene/ethylene (weight ratio)	0.4	0.6	0.3	0.5	0.03
Propylene (weight percentage of C_3)	98.3	96.7	58.3	99.0	86.7

1.2.2 Fluid catalytic cracking (FCC)

Propylene is produced in refineries from three main processes: fluid catalytic cracking (FCC), delayed cookers and thermal cracking [2]. FCC represents the major producer of propylene in the refineries as a co-product to gasoline [3]. FCC is the largest refining unit that produces gasoline with a world capacity of more than 14.2 million bbl /day (715 million tons per year). 60% of propylene production from FCC used in petrochemical and chemical production and about 40% is used in producing high octane gasoline blends by converting the propylene to alkylate which have high octane number through alkylation process [3, 10].

The main FCC sections are reactor (riser), stripper, catalyst regenerator, fractionator, and system for feed injection. Fluid refers to a fluidized catalyst that flows from the reactor to the regenerator and back. Fluidized beds usually have lower pressure drop than down flow at high flow rates. Fluidizing the catalyst also makes it easy to move from one reaction zone to another. Spent (coked) catalyst flows to the regenerator to burn off the coke with hot air to restore catalyst activity. FCC reactions are mainly endothermic; the heat balance is obtained by the regenerator where the deposited coke burned in high temperature. Figure 1.6 shows the flow diagram of FCC unit [3].

FCC is used to convert the heavy oil feedstocks like residue and vacuum gas oil into gasoline and other lighter products (C_1 - C_4 products). Propylene produced from FCC is about 5 -19% in volume of the feed. To get a high yield of light olefins specially propylene the feedstock sulfur content should be decreased while the hydrogen content should be increased, this can be done by using a high performance hydrotreaters before FCC unit to remove sulfur or lower sulfur feedstock.

Currently it is not economically feasible to build FCC unit mainly for propylene production due to low yield of propylene, so the focus of recent research is increasing the yield of propylene; which depends on many variables such as reactor type, operating conditions (temperature, pressure and recycle ratio), feed composition and the catalyst. The recent catalyst significant development has increased the yield by more than 10%, also some catalyst additives are used to boost the yield [3, 10].

Table (1.3): The product yield in a typical FCC unit vs other similar technologies [3]

Parameters	Fluid catalytic Cracking (FCC)	Deep Catalytic Cracking (DCC)	Petro FCC	High Severity (HF-FCC)
Reaction temperature (°C)	500	530	590	600
Product yield (wt %)				
Ethylene	1.5	5.4	6.0	2.3
Propylene	4.8	14.3	22.0	15.9
Mixed butanes	6.9	14.7	14.0	17.4
Gasoline	51.5	39.0	28.0	37.8
Heavy and light oils	21.0	15.6	14.5	9.9
Coke	4.5	4.3	5.5	6.5

According to the high demand of gasoline comparing with propylene, most of the FCC technologies are not interested in increasing the capacity of propylene production. So, we need to focus more on the on-purpose propylene production technologies.

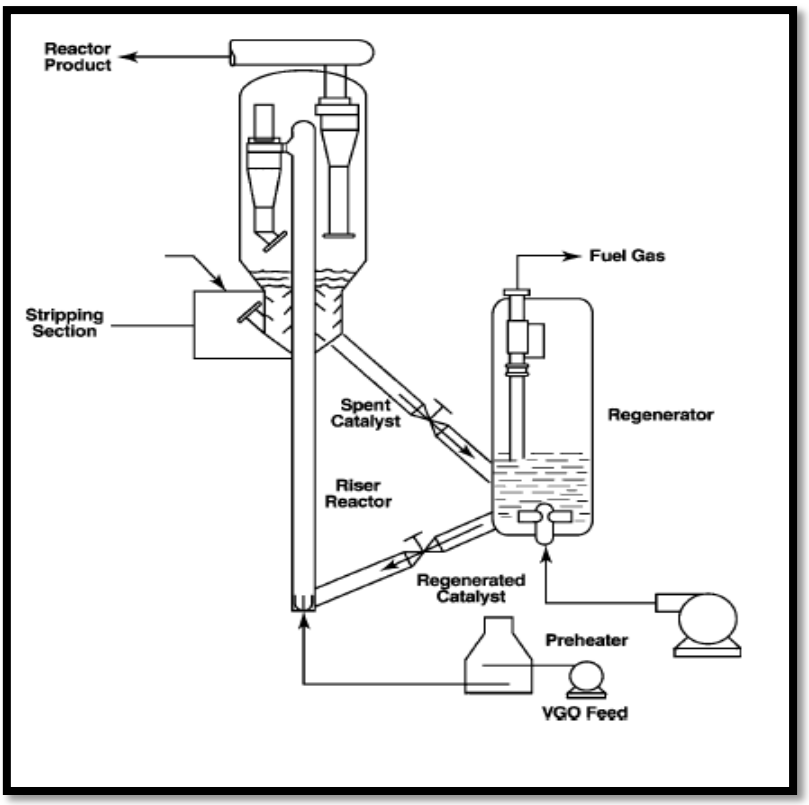


Figure (1.6): FCC unit flow diagram [3]

1.2.3 Propane Dehydrogenation (PDH)

Due to increasing demand of propylene, propane dehydrogenation has a great interest as an alternative method for production. It is a catalytic process to convert the propane (produced from natural gas of refining process) to propylene by separating hydrogen.

$$C_3H_8 \longrightarrow C_3H_6 + H_2 \qquad (\Delta H_{r,\,298\,K} = 129.4\ kJ/mol) \qquad (1.1)$$

Propylene yield from this process is about 85%. Hydrogen is produced as a co-product and is used as a fuel for the process. The favorable operating conditions are high temperature and low pressure to get a good conversion. Due to endothermic nature of propane dehydrogenation process noble metals have been employed as a catalyst for this process due to their high activity. One of the problems of these

catalysts is the fast deactivation, as a consequence this process needs at least two fixed bed reactors one for the reaction and another for the regeneration.

PDH have limited activity due to the availability of feedstock and the cost so, it will be very difficult to cover the increasing consumption of propylene by propane dehydrogenation [3, 8].

1.2.4. Conversion of Methanol to olefin (MTO) and Methanol to propylene (MTP)

The Methanol to olefin process (MTO) was discovered in 1977 by Mobil oil [3]. This process is used to produce olefins such as ethylene and propylene and also to produce gasoline from methanol (obtained from natural gas and coal). Availability of low cost feedstock such as methanol with increasing demand for propylene makes the conversion of methanol to olefin (MTO) and methanol to propylene (MTP) economically feasible. These two processes are available for propylene production for many years and created big companies like (UOP) which is developing methanol to olefin (MTO) and Lurgi which is developing methanol to propylene (MTP) [3]. The two processes begin from transferring the natural gas to methanol and then to light olefin. Usually, this process is catalyzed by acidic zeolite catalysts, without these catalysts, the chemical reactions of the (MTO) process would be very slow; thus affecting the process [3, 8].

1.2.5. Olefin Metathesis

Metathesis is a reversible reaction between two olefins to break the double bonds of olefins and form new olefin products. Propylene is produced commercially via metathesis by combining a molecule of 2-butene and a molecule of ethylene to form two molecules of propylene.

$$CH_2 = CH_2 + CH_3\text{-}CH = CH\text{-}CH_3 \rightleftharpoons 2\ CH_3\text{-}CH = CH_2 \qquad (1.2)$$

(Ethylene) (2-Butene) (Propylene)

Olefin metathesis is a process that produces propylene from ethylene and butenes in the presence of catalysts. Metathesis unit is combined with the steam crackers unit to increase the propylene production by the transformation of ethylene and mixed butenes. Figure 1.7 shows the flow diagram of metathesis process. There are more than 20 commercial metathesis OCT Lummus plants (2010) in the world. Two additional plants have been built by the end of 2015. Most of the global propylene production through metathesis is from Asia and Middle East region derived by upgrading low valuable products to high valuable ones [8].

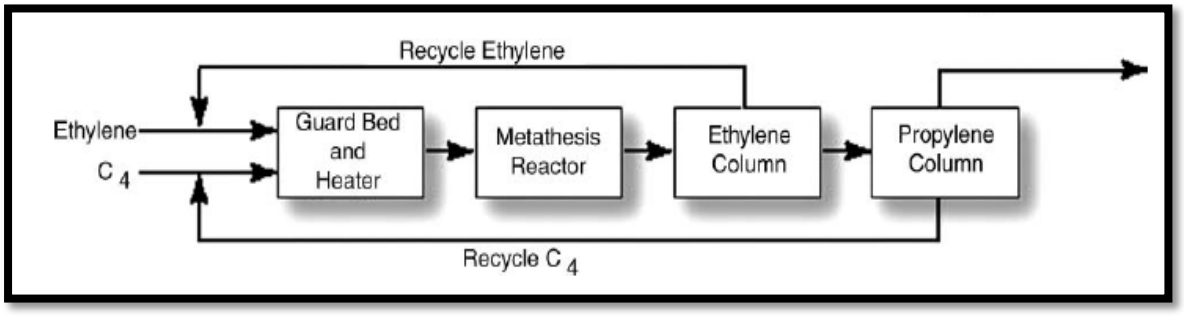


Figure (1.7): Metathesis flow diagram [3]

In this research, one of the main objectives is to convert low valuable C_5 olefins to more valuable product through olefin metathesis. In literature review, historical perspective of C_5 metathesis is included with emphasis on basic chemistry and reaction mechanism, catalysts employed in C_5 conversion and other technologies that could be used in C_5 conversion reaction mechanism are highlighted.

1.2.6 Olefins Cracking

Olefin cracking (olefin interconversion) is based on C_5 and C_4 catalytic cracking. The process is comparable with FCC and ethylene cracking and doesn't consume much ethylene like olefin metathesis.

Olefin cracking unit is preferably added also to steam crackers unit or FCC unit. Most of the commercial processes use shape-selective zeolitic catalysts with medium-pore cracking of olefin stream to ethylene and propylene in a fluidized-bed reactor.

Lurgi improved a catalytic process with low pressure called (Propylur) that uses adiabatic fixed-bed technology for transforming olefins stream to propylene and ethylene in the presence of steam. There are other technologies such as "Atofina/UOP's olefin cracking process, Lyondell /Kellogg's fluidized-bed Superflex process, Linde's fixed bed catalytic cracking (FBCC), and Exxon Mobil's olefin interconversion (MOI) [3].

1.2.7 Conclusion

Propylene is mainly produced as a co-product from steam cracking of naphtha, FCC of gas oil in refineries and low quantities from propane dehydrogenation (PDH) and olefin metathesis. To fill the gap between supply and demand of propylene, research

is still in progress to find new on-purpose technologies like olefin interconversion, hydrocarbons catalytic cracking and methanol conversion to increase the propylene yield. The yield depends on operating conditions (temperature and pressure), feed composition and the catalyst. Table (1.4) shows selection standard for on-purpose processes for propylene production. [3]

Table (1.4): Standard of selection of technologies used in propylene production [3]

Selection Standard	**Deep Catalytic Cracking (DCC)**	**Dehydrogenation**	**Metathesis**	**Olefin Cracking**	**MTO/ MTP**
Feedstock	Gas Oil	Propane	C2-C4 olefins	C4-C8 olefins	Methanol
Steam Cracker Integration	No	No	Yes	Yes	No
Investment	Moderate	High	Moderate	Moderate	Very High
Commercial units	Several	Several	One	None	None

1.3 Thesis Objectives

The overall objective of the proposed study is the development of novel catalysts for conversion of C_5 olefins to more valuable product (propylene) by metathesis reactions.

Main objective

- Conversion of C_5 olefins to propylene by metathesis reactions.

Tasks to achieve this objective

- Develop metathesis novel catalysts supported on conventional silica, mesoporous materials and microporous materials.

- Characterize prepared catalysts by physicochemical methods (XRD, N_2 sorption and ICP-OES) to determine catalyst structure and the quality of metals used.

- Evaluate catalysts for metathesis reaction of C_5 olefins in a fixed bed reactor.

- Optimize reaction conditions (temperature and catalyst/feed ratio) to achieve higher yield for propylene by experimental work.

CHAPTER 2

LITRETURE REVIEW

2.1 Introduction

Major source of olefin in gasoline is Fluid Catalytic Cracking (FCC) unit. However, Refiners have to meet increasingly stringent specifications for cleaner gasoline defined by the Worldwide Fuel Charter (WWFC), a global agreement between the major motor manufacturers in the US, Europe and Japan. Therefore Olefin metathesis and olefin cracking are frequently used for upgrading olefins from oil refinery products [12]. According to the market situation, the less valuable olefins especially C_5 can be transformed by metathesis and cracking to the more valuable ones (propylene and ethylene). Increasing demands on ethylene and propylene led to the increased interest in their production from longer chain olefins by metathesis and cracking [13]. On the other hand, prolongation of olefinic chains by metathesis has been employed e.g. in production of detergent range hydrocarbons [13-15].

2.2 Olefin Metathesis

2.2.1 Background

Olefin metathesis is a process that produces propylene from ethylene and butenes in the presence of catalysts. Metathesis unit is preferably added to steam crackers unit to increase the propylene production by the transformation of ethylene and mixed butenes. Olefin metathesis represents an important reaction in upgrading of less

valuable olefins into desired ones and has numerous industrial applications (e.g. Philips triolefin process, Shell higher olefin process, neohexene process etc. [30, 31]. Commercially There are more than 20 metathesis OCT Lummus plants (2010). Two additional plants have been built by the end of 2016.

Successful synthesis of mesoporous molecular sieves, originally as silicates and aluminosilicates have opened a new area in material research [19]. Rapid development of new synthetic pathways delivered numerous structures of different architecture and pore size. Hexagonal MCM-41 with pore diameter d = 4 nm, SBA-15 with d = 6-11 nm and cubic MCM-48 with d = 3-4 nm belong to the most frequently used materials. Mesoporous molecular sieves represent advanced material for sorption and catalysis because of having large surface areas (up to 1000 m^3/g) , high void volumes (up to 1 cm^3/g) and narrow pore size distributions in mesopore dimensions (i.e. 2-30 nm) [20, 21]. They have also been used as supports for advanced metathesis catalysts [22]. Hierarchical materials or two-dimensional zeolites, combining large BET areas and easy accessible active sites offer similar properties as mesoporous molecular sieves [23, 24]. Two important groups of zeolite-based supports with mesoporous features were discovered recently i.e Two-dimensional zeolites and Mesoporous zeolite. Two-dimensional zeolites were prepared directly [25, 26] or by post-synthesis treatments [27]. Mesoporous zeolite single crystals were prepared by direct synthesis using secondary templates [28] or by post-synthesis desilication [29]. Primary importance of these materials is having large BET areas reaching even 900 m^2/g for delaminated materials or highly accessible mesopores in the case of pillared materials. We believe that these materials can also be promising candidates for supports of advanced metathesis catalysts.

Balcar and Cejka [33] have reported use of siliceous mesoporous molecular sieves (MMS) such as MCM-41, SBA-15, MCM-48 and organized mesoporous alumina (OMA) supports to develop new heterogeneous catalysts for olefin metathesis. It was observed that with Mo and Re oxides these new supports provided catalysts of higher activity comparing to those based on conventional silica and alumina. Immobilization of Mo and Ru alkylidines on these materials led to catalysts with high activity and selectivity with negligible leaching of transition metal.

Ookoshi & Onaka [34] have reported new hexagonal mesoporous silica (HMS) for molybdenum-based olefin metathesis catalyst. This catalyst exhibited superior catalytic activity for the metathesis of 1-octene in liquid phase compared to MoO_3 on normal porous silica and MoO_3 on gamma alumina. A similar enhancing effect on the catalyst activity was observed for MoO_3 supported on mesoporous molecular sieves MCM-41, MCM-48 and SBA-15 [35, 36]. In metathesis of neat 1-octene, 7 times higher activity was found for MoO_3 on MCM-41 in comparison with MoO_3 on conventional silica. 75 % conversion to 7-tetradecene was achieved at 40°C (6 wt. % Mo loading, 6h, batch reactor).

Recently Bhuiyan et. al [37] have reported; metathesis of 2-butene using WO_3 supported MCM-41 and SBA-15 catalysts in a fixed-bed reactor. The WO_3-MCM-41 exhibited highest propylene yield of 39 mol %.

Good dispersion of metal oxide on the support surface is considered to be a crucial factor for obtaining a highly active catalyst. In this regard, Handzlik et. al [38] have reported molybdena-alumina catalyst, prepared by anchoring of $MoO_2(acac)_2$ complex. This catalyst displayed much higher activity during propylene metathesis reaction as compared to that of traditionally impregnated molybdena-alumina catalyst.

Debecker et. al [39] have reported preparation of MoO_3 /SiO_2-Al_2O_3 via flame spray pyrolysis. This catalyst was observed having highly dispersed and highly active molebdate species for metathesis reaction of propylene. Raman spectra showed that only isolated MoO_x species covalently bound to the surface Si atoms, are able to give rise catalytically active species (i.e. surface carbenes) during the catalyst activation process [40]. Mesoporous molecular sieves having high BET areas can ensure a better dispersion than ordinary silica.

Thermal spreading was found as an easy and very effective method for MoO_3 supporting on mesoporous sieves [36]. To further increase the population of isolated MoOx species on the support surface, various mono- and dinuclear Mo complexes with organic ligands (like acetate, acetylacetonate, oxalate, glycolate) were investigated as a source of Mo carbenes [27, 30, 31]. The complexes were deposited on the surface either from solutions or by thermal spreading. In all cases, highly dispersed MoO_x species were formed after calcination and catalysts obtained exhibited a high activity. In the case of MoO_2 $(acetylacetonate)_2$ and MoO_2 $(glycolate)_2$ supported on SBA-15, the catalytic activity in 1-alkene metathesis was significantly higher than that achieved over corresponding catalyst prepared by thermal spreading of MoO_3 [43].

Recently, attempts to prepare mesoporous metathesis catalyst by direct sol-gel synthesis have been made [37, 44, and 45]. Instead of supporting a transition metal compound on a mesoporous support; a direct hydrothermal synthesis from a mixture of a suitable transition metal compound (Ru complexes, sodium tungstate) and a water soluble Si source like sodium metasilicate or tetraethoxysilane (TEOS) was accomplished. High activity of mesoporous catalysts was ascribed to the better

dispersion of active species on the surface in comparison with that achieved by using already made support. In addition, one step synthesis may be easier and less expensive. Mesoporous silica (MCM-41 and SBA-15 type) having tungsten oxide in the framework was successfully prepared and exhibited higher activity as compared to tungsten oxide impregnated catalysts [37]. On the other hand, similar molybdenum oxide catalyst has not yet been reported in the literature.

2.2.2 Basic Chemistry of Metathesis and reactions mechanism

Metathesis is a reversible reaction between two olefins to break the double bonds of olefins and form new olefin products. Propylene is produced commercially via metathesis by combining a molecule of 2-butene and a molecule of ethylene to form two molecules of propylene.

$$\underset{\text{(Ethylene)}}{CH_2 = CH_2} + \underset{\text{(2-Butene)}}{CH_3\text{-}CH = CH\text{-}CH_3} \rightleftharpoons \underset{\text{(Propylene)}}{2\ CH_3\text{-}CH = CH_2} \qquad (2.1)$$

There are two major reactions in C_5 olefin metathesis (self-metathesis and cross-metathesis) and other side reactions mainly isomerization. 2-$C_5^=$ undergo self metathesis to produce 2-butene and 3-hexene. 2-$C_5^=$ undergo isomerization to produce 1-$C_5^=$ and then react with each other for cross metathesis to produce propylene and 3-heptene.

According to the mechanism of olefin metathesis, some reactions have very low productivity such as 2-butene self-metathesis, ethylene self-metathesis and reaction of 1-butene or isobutene with ethylene. Figure 2.1, figure 2.2 and figure 2.3 show the metathesis reactions (self-metathesis, cross metathesis and isomerization) of C_5 olefins [12].

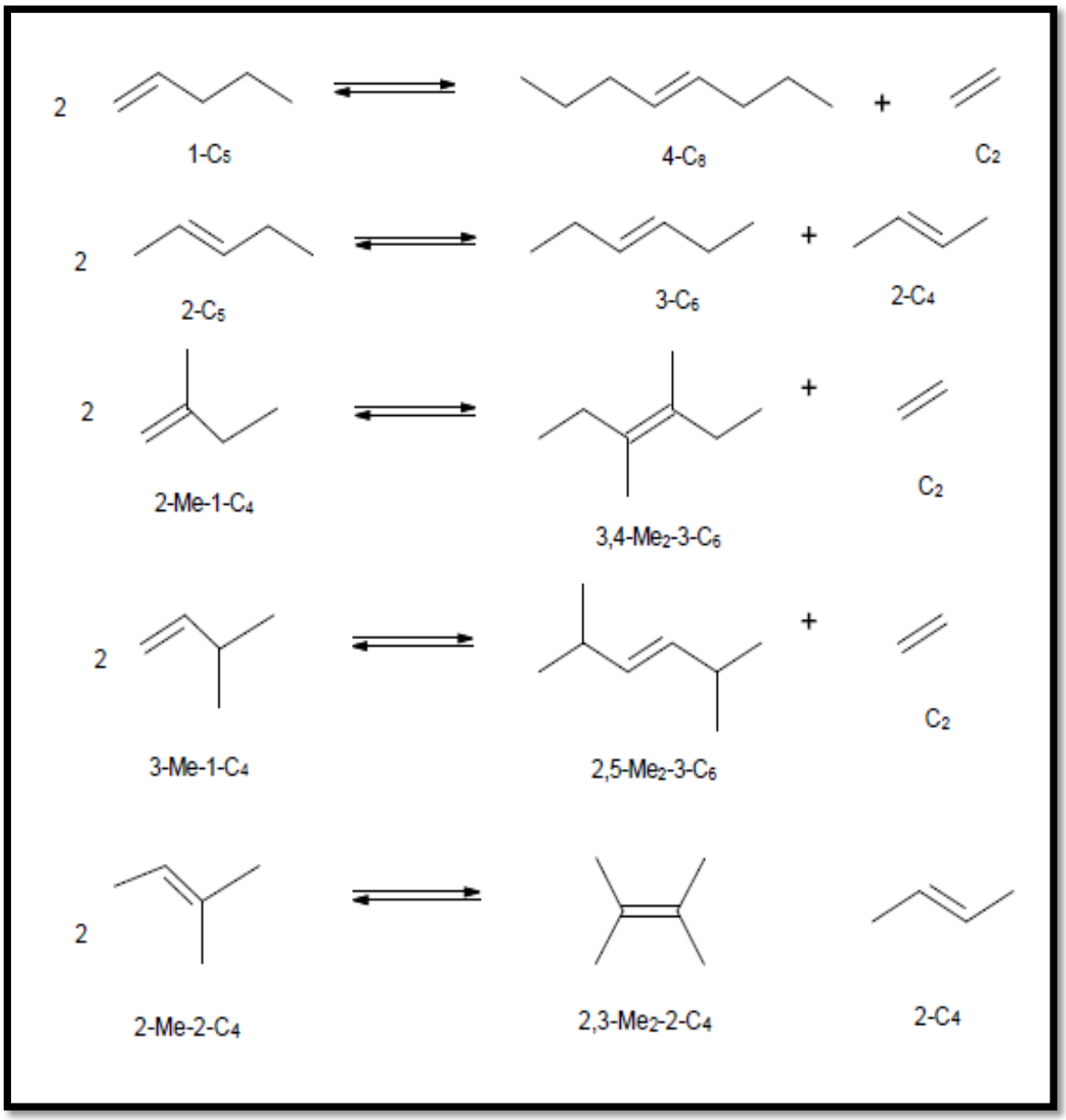


Figure (2.1): Self-metathesis reaction of C_5 olefins

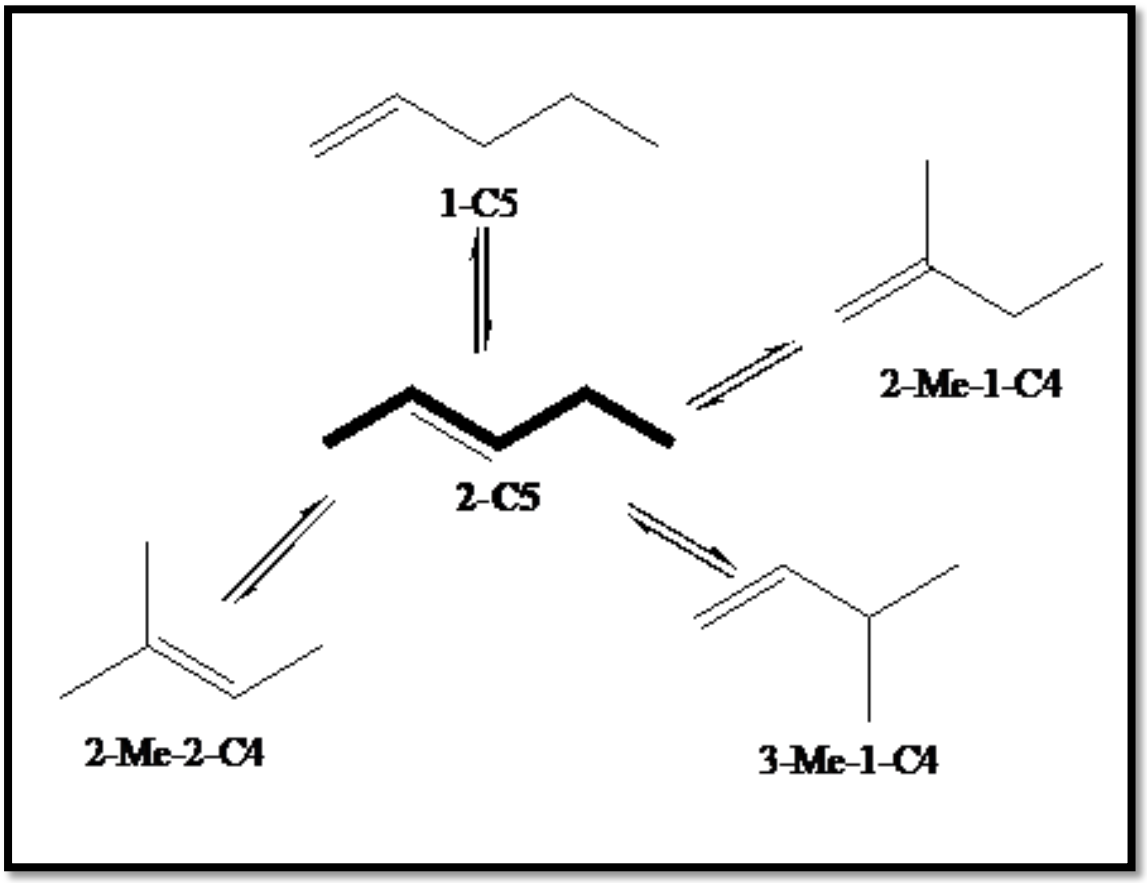


Figure (2.2): Isomerization reaction of C_5 olefins.

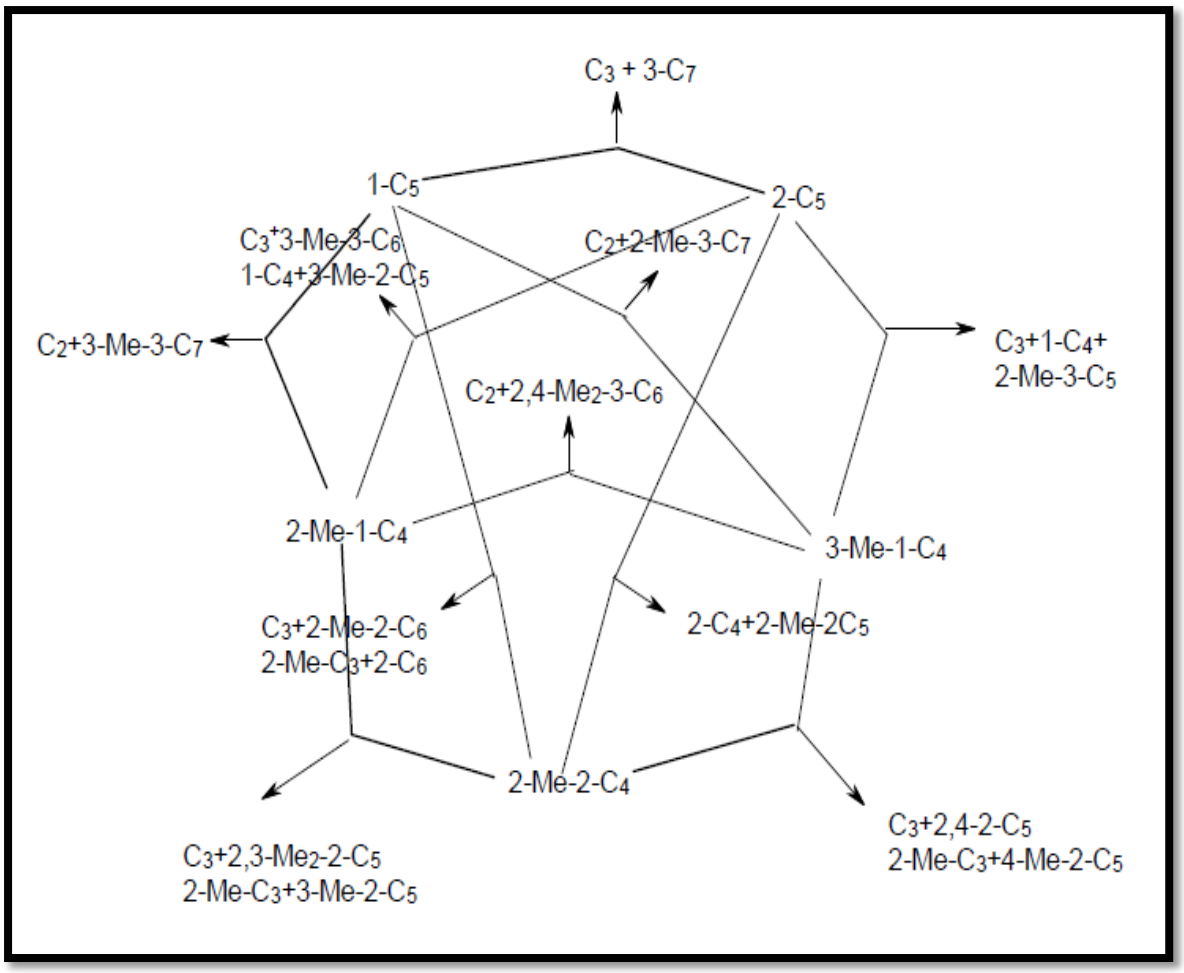


Figure (2.3): Survey of cross-metathesis reactions in C_5 olefin mixture

In hydrocarbon formula (x-Me-y-C_n) where:

x = position of methyl substituent.

y = position of the double bond.

n = number of carbons in the main chain.

2.2.3 Metathesis Catalyst

2.2.3.1 Metals used for metathesis reaction

Both heterogeneous and homogeneous catalyst can catalyze the reactions of Metathesis and can form complex of metal-carbene to form metallacyclobutane intermediate.

A variety of metals which are employed for metathesis reactions are highlighted in periodic table (Figure 2.4). However, these metals (Mo, W, Ru and Re) are the most active ones.

Homogeneous catalysts consist of either a well characterized carbene complex of transition metal (e.g. Ru, Mo or W) or a combination of transition metal compound [usually an (oxo) chloride)] or an organometallic compound as co-catalyst. These homogeneous catalysts have a good perspective for polymerization. On the other hand, heterogeneous catalysts are more useful for petrochemical and organic synthesis

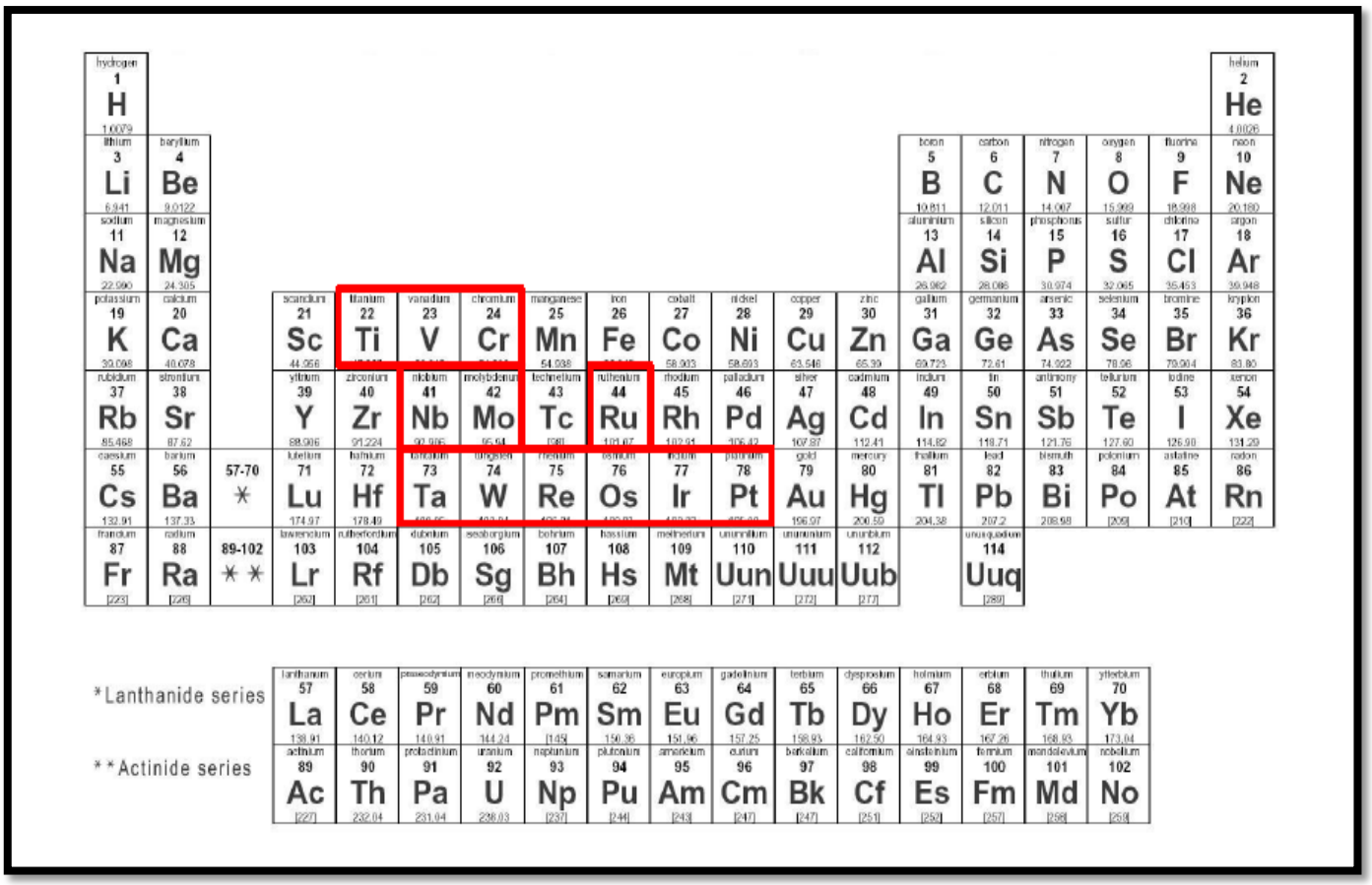


Figure (2.4): Metals used in Metathesis reaction (Periodic Table).

Heterogeneous catalysts used for these applications are based on molybdenum, tungsten, rhenium and ruthenium oxide supported on alumina or silica. Catalysts based on Molybdenum and Tungsten oxide require higher temperatures, where metathesis selectivity decreases due to side reactions. Only catalysts based on Rhenium oxide show high selectivity and activity at low temperature (below 100ºC), but with low loading (<10wt %) of Rhenium which is very poor; the catalysts are deactivated very fast. On the other hand, cost of rhenium compounds is very high. Figure 2.5 shows the reactivity of metals used in metathesis.

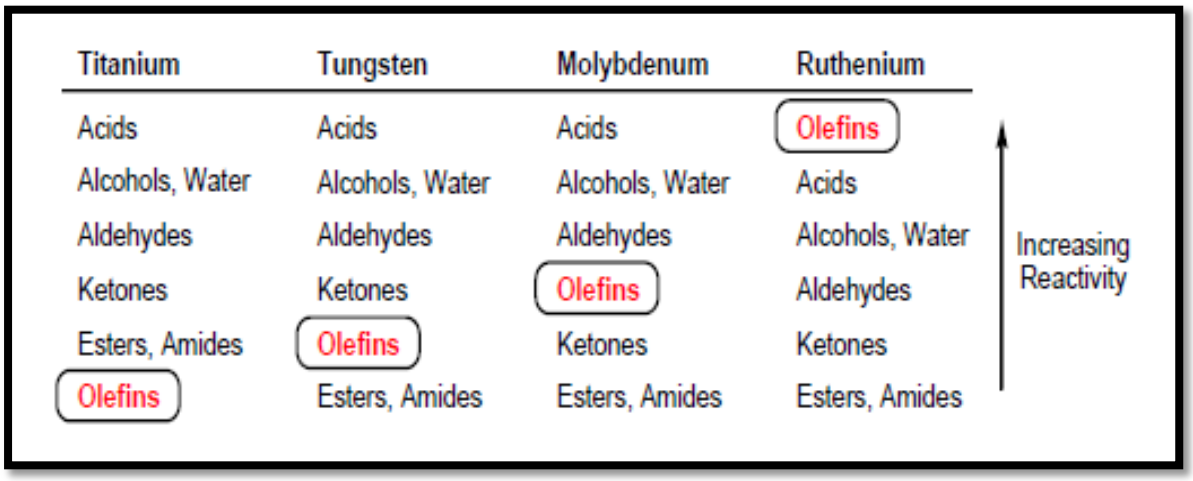


Figure (2.5): Reactivity of metals that used in metathesis in different groups

Mo oxide catalysts with alumina, siliceous material, silica alumina support and zeolite alumina composite support have been frequently used for petrochemical applications due to their high activity at room temperature and relatively low prices but have some limitation and require pure feed. In contrast, the tungsten based catalysts also display a good activity and selectivity. They are flexible to frequent poisoning and also enable continuous regeneration of the catalyst without negative effects on the catalyst structure. All of that make the tungsten based catalysts most attractive for commercial use. Tungsten oxide catalysts require high temperature (250-500°C) to attain appreciable activity which depends on the oxidation state, tungsten oxide content, the support properties and the conditions of pretreatment.

In conclusion, W and Mo heterogeneous catalysts still remain the most important industrial metathesis catalysts and still attract the attention of researchers (in both academic and applied research) aimed at improving efficiency of these catalysts. Figure 2.6 shows the metal used in metathesis catalysts.

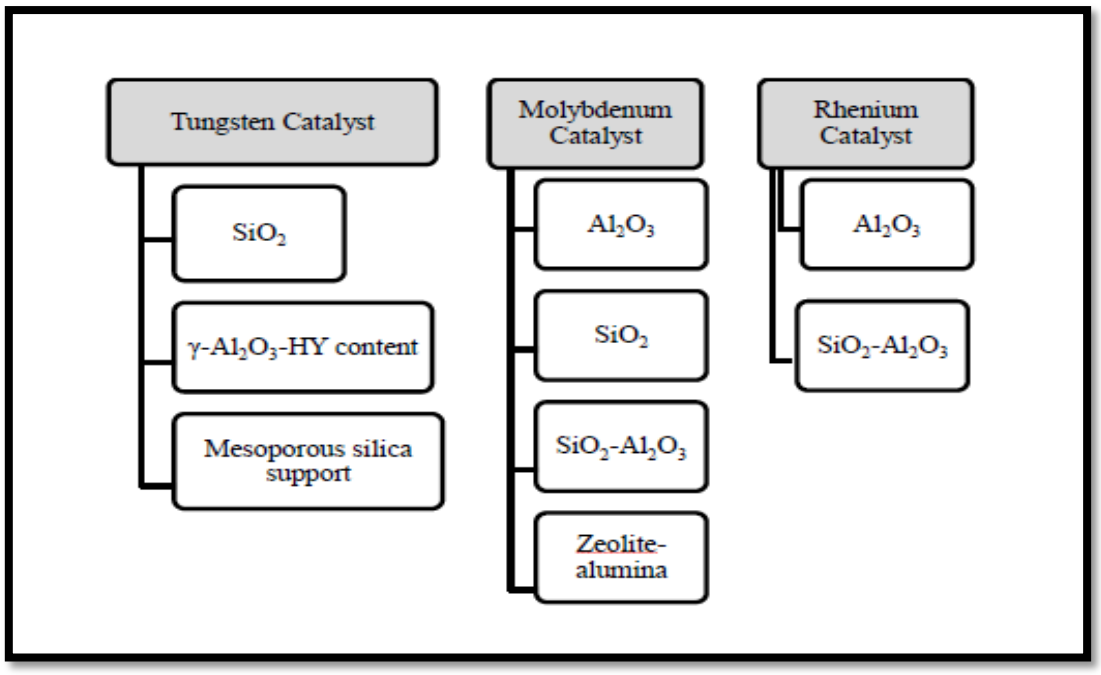


Figure (2.6): Metal based catalyst with different types of supports used in metathesis

2.2.3.2 Mesoporous support (SBA-15 & MCM-41)

Porous materials commonly used as catalysts and catalyst supports. These porous materials are divided into three types according to the pore size definition of IUPAC (International Union of Pure and Applied Chemistry); microporous materials (pore size < 2nm), mesoporous materials (2‑50nm) and macroporous materials (>50nm).

MCM-41 is a common mesoporous material. "It is usually synthesized by a templating mechanism. Through phase separation, a continuous network surrounding template molecules is formed first. Then, by combustion and /or extraction, the template is removed, leaving the empty space inside the network material as mesopores".

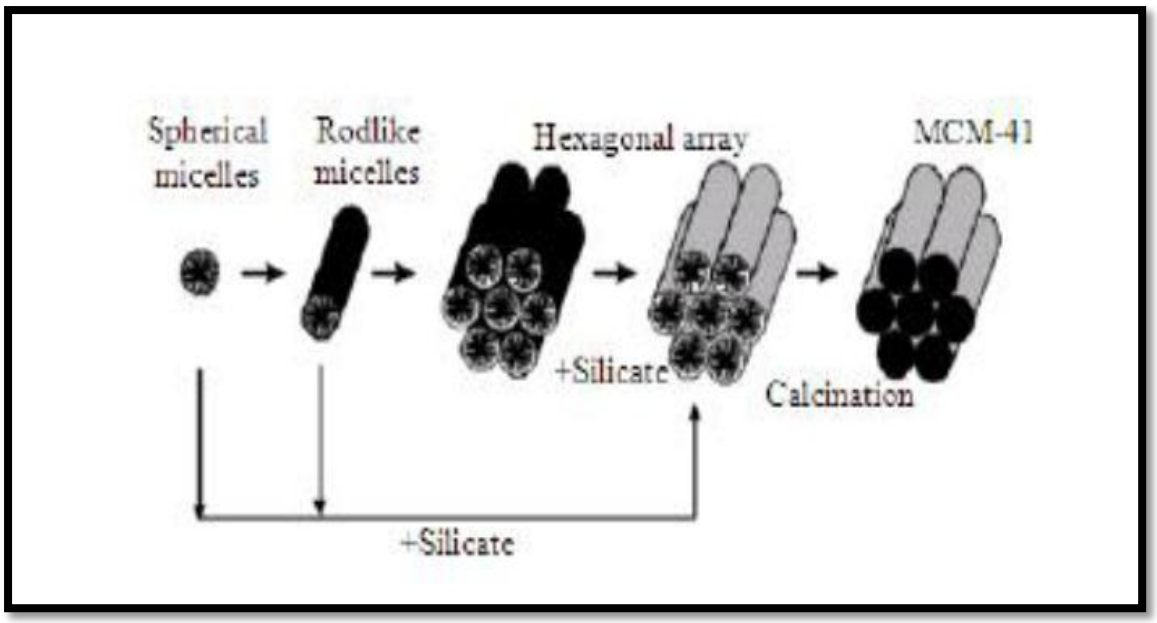


Figure (2.7): Typical synthesis of mesoporous silica MCM-41

Recently SBA-15 has become an important catalyst in many areas not only because of its larger pores (5-30 nm) but also it has mechanical, thermal, hydro-thermal strength due to its thick framework walls (3-6 nm). The mesopore diameter of SBA-15 depends on the synthetic conditions: increasing the gel aging temperature leads to a larger pore diameter. One interesting feature of SBA-15 is the microporosity present in its mesopore wall, by which the micropores connect neighboring mesopores.

Figure (2.8): Pores network connectivity in SBA-15 support. [49]

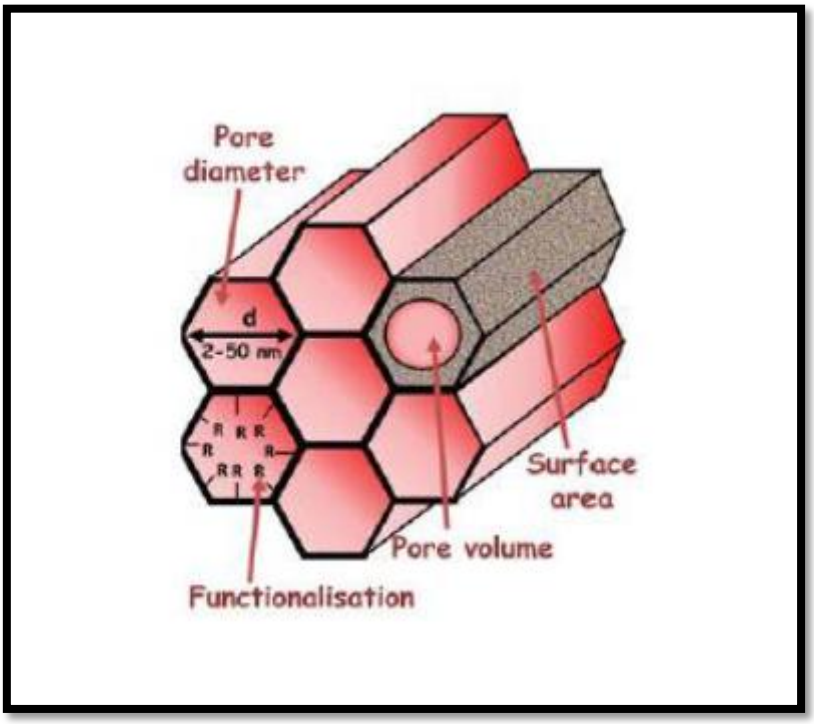


Figure (2.9): SBA-15 support properties (pore volume, surface area and pore diameter) [50]

2.2.4 Experimental plan

2.2.4.1 Catalyst preparation Plan

Metal oxide have been supported on three types of supports such as conventional silica (SiO_2), mesoporous supports (MCM-41 and SBA-15) and microporous supports (MCM-22). Mesoporous molecular sieves MCM-41 and SBA-15 were prepared using hexadecyltrimethyl ammonium bromide and Pluronic PE 9400, respectively. Selected 2D zeolites based on the structural types of MWW and MFI were prepared, fully characterized and used for immobilization of active metathesis species.

Two methods of metal oxide introduction were used such as thermal spreading method and wet impregnation method with different metal oxide loading.

2.2.4.2 Catalyst testing Plan

The majority of tests were done in flow system in a mixture of liquid ($C_5^=$) and gaseous phase (N_2). Catalyst activation before reaction was performed in a stream of nitrogen at 550°C. Reaction products were analyzed by GC and GC-MS. The changes of catalyst activity with time were examined. The possibility of used catalyst regeneration (by heating in air flow at high temperature) was tested.

2.2.5 Research methodology

The proposed research work will utilize the recent literature results in synthesis of mesoporous sieves and development of metathesis catalysts. Novel Mo oxide based catalysts on advanced supports (mesoporous molecular sieves and 2D zeolites) were developed. It is expected that these catalysts will operate at lower temperature than WO_3 based catalyst and will exhibit also higher selectivity. The effect of support

structure on catalyst activity and selectivity will be established. Until now 2D zeolites have not been used as a support for metathesis catalyst, therefore during this project the advantages of these new supports will be practically verified and possible limitation revealed. Using literature data concerning preparation of Ru and W catalyst a new way to the mesoporous Mo-oxide catalyst by direct sol-gel process will be investigated. If the prepared catalysts exhibit desired activity this method will represent an easier and less expensive method for advanced Mo oxide catalyst preparation.

The optimization of catalyst activation and reaction conditions as well as the investigation of catalyst stability and susceptibility to poisoning effect of impurities in reactants will contribute to the catalyst efficiency.

The application of metathesis leads to the transformation to light olefins (ethylene, propylene, butane) on one side and to the formation higher alkenes (mostly branched heptenes and octenes) on the other side (see figure 2.1) for self-metathesis product and figure (2.3) for all possible cross-metathesis products). The detailed product composition depends both on the feed composition and on the catalyst selectivity, especially on the presence of isomerization and oligomerization reaction. The latter will be controlled by the proper catalyst choice.

2.3 Cracking

2.3.1 Background

Cracking is a Breaking of large, long chained hydrocarbons into small, short chained molecules which are more valuable and suitable for further processing. Propylene can be produced by cracking C_5 olefins. The process can be used in steam cracking plants or FCC units in order to enhance propylene yield. The olefins cracking reactions are accompanied with oligmerization reactions, isomerization and hydrogen transfer reactions. To increase propylene yield, hydrogen transfer reactions and cyclization reactions should be minimized; because these reactions lead to the formation of paraffins and aromatics [3].

2.3.2 Basic Chemistry of Catalytic Cracking

Cracking is one of the significant reactions to convert C_5 olefins to valuable products. It is one of the hydrocarbon reactions that are catalyzed by acid catalysts (zeolites). Figure (2.10) shows the main reactions for acid catalyzed reactions.

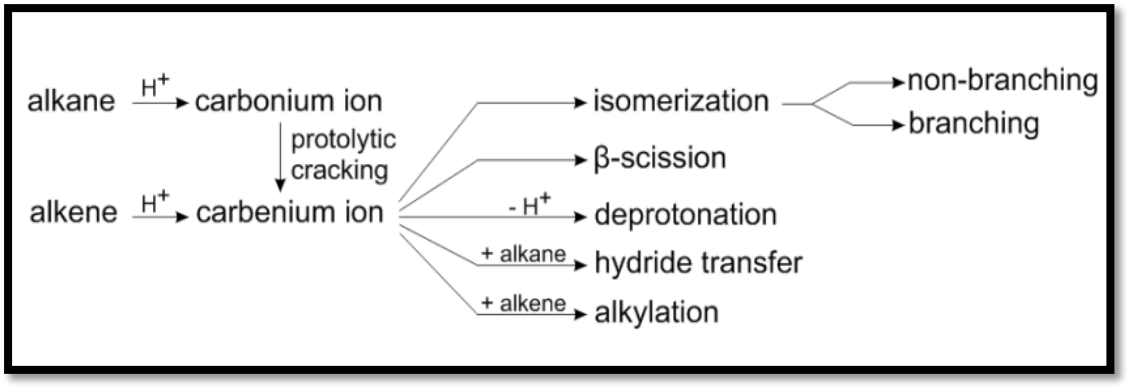


Figure (2.10): Scheme of the main reactions involved in alkene catalytic cracking.

Alkane protonation yields a carbonium ion, which can be cracked protolytically to form carbenium ion, while alkene protonation also yields carbenium ion directly. Figure 2.5 shows the difference between carbonium and carbenium ions. These carbocations go through further reactions such as isomerization, β-scission, deprotonation, hydride transfer and alkylation [11].

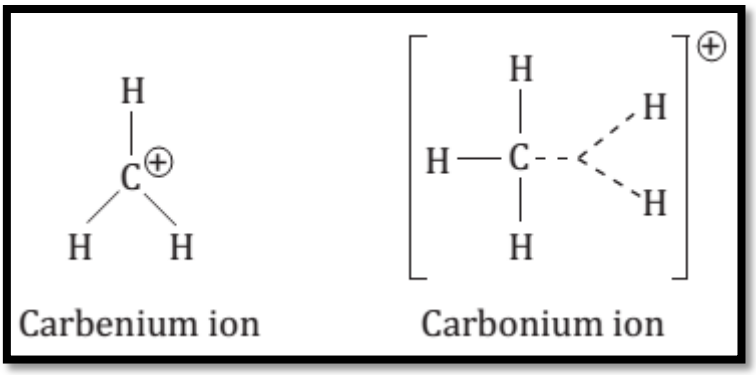


Figure (2.11): Carbenium ion and Carbonium ion [11]

2.3.3 Cracking Catalysts

Zeolites are the most significant type of catalysts used for cracking. These are highly crystalline materials which consist of SiO_4 or AlO_4 tetrahedra with Si or Al atom at the center (termed TO_4) which gives three dimensional molecular sieve structures. Exchange of silicon atoms with trivalent aluminum atoms resulted in a negative charge in the framework; this negative charge is stabilized by cationic species. Cationic species are exchanged by protons forming Brønsted acid sites, and are considered as the sites responsible of catalytic cracking.

Table (2.1): Common Zeolites catalysts used in olefins cracking

Catalyst	**Si /Al ratio**
H-ZSM-5 (23)	23
H-ZSM-5 (80)	80
H-ZSM-5 (280)	280
H-ZSM-5 (1500)	1500
Silicalite-1	> 1800
Mordenite	180
β – Zeolite	38
β – Zeolite	300

CHAPTER 3

EXPERIMENTAL

3.1. Experimental Setup

3.1.1. Fixed bed tubular reactor system

The reaction system is a complete reaction microsystem for the evaluation of the catalyst while analyzing the data in continuous flow process. Fixed bed tubular reactor along with a thermostat is fixed in a tube furnace heater. The temperature in the furnace and the reactor are controlled with two thermocouples. The reactor and furnace are placed in an isothermal oven. This oven is heated using a forced convection blower to reduce unwanted condensation. The multi-port reactor status valve can allow the bypass of the reactor. This valve gives an appropriate means of conducting analytical sampling of the inlet material without passing through the reactor. Mechanical gauge and digital pressure transducer are used to measure pressure at the reactor inlet. The gauge and the transducer are insulated with silicone-filled isolator with a welded stainless steel diaphragm. Back pressure controller is used to maintaining the pressure. Pressure digital indication is also provided. Figure (3.1) showed the major components of the reaction system.

Up to six inputs can be handled in the reactant preparation section; two of these inputs are liquid pumps for liquid feeds with high pressure and the other four are mass flow controllers for gas feeds. The reactants are mixed and vaporized to create a non-fluctuating homogeneous stream which is then sent to the reactor.

Figure (3.1): Fixed bed tubular system

Before sending the feed to the system its flow is controlled with high pressure metering valves, in-line filters, reverse-flow check valves, thermal mass flow controller and a 2 or 3-way diverter valve.

The vapor phase effluent from the reaction system is transferred to a customer-supplied gas chromatograph through a heated transfer line. This transfer is controlled by a heated multi-port sampling valve which is placed inside the isothermal oven.

Three adjustable PID controllers are part of the system control; they are used to control the temperature of the reactor, oven and the transfer line. Also, the multi-port reactor status and the sampling valves are allowed to rotate. The risk of hazardous over pressurization is eliminated by using a rupture disk. The multi-port reactor status valve permits the reactor purging throughout shutdown. Some individual temperature controllers allow power termination to any heater station with a burned-out or sensor. A schematic diagram of experimental setup is shown in Figure (3.2).

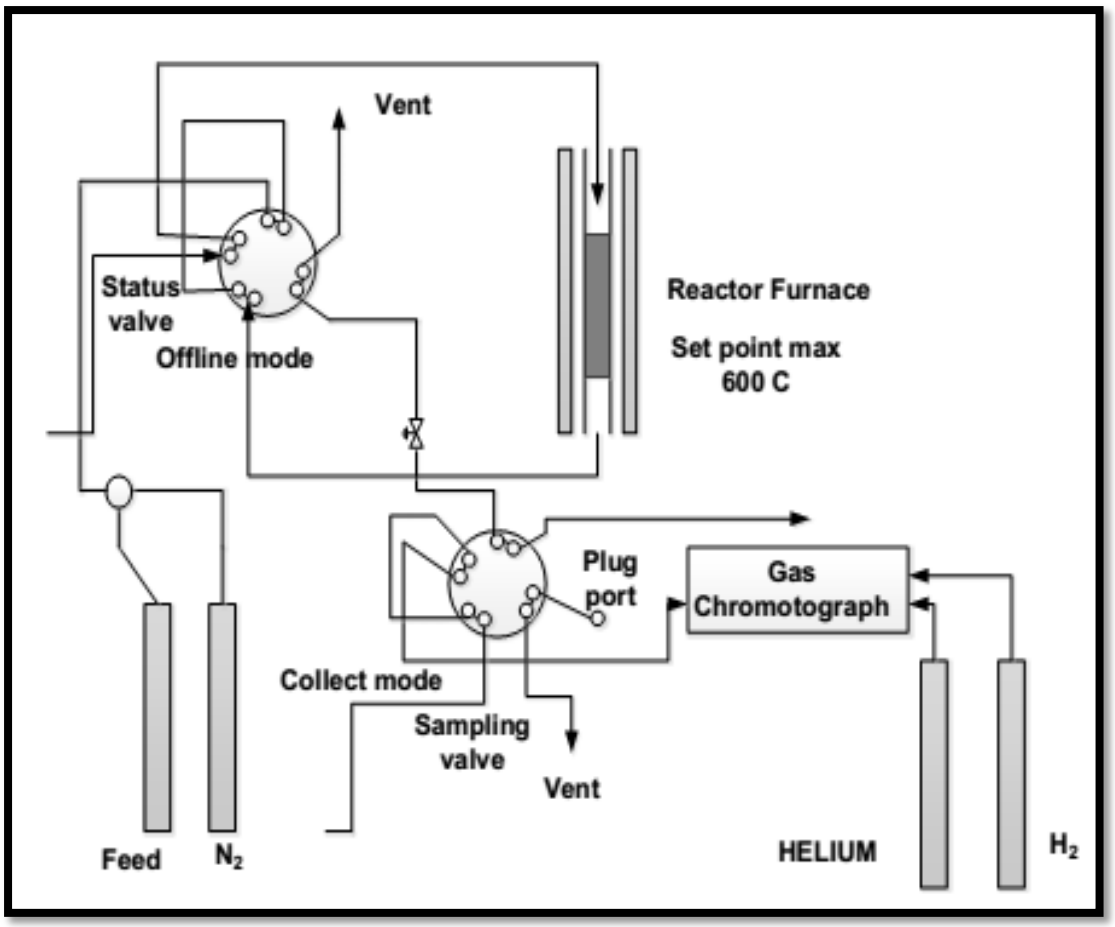


Figure (3.2): Schematic diagram of the fixed bed tubular reactor

3.1.2. Gas Chromatographic (GC) system

The quantitative analysis of the products of the reaction was conducted using Varian GC with FID (Varian 450-GC), equipped with two FID. FID1 A (front channel) (Column Gas-pro, (60m x 0.320 mm)) and FID2 B (back channel) (Column Gas-pro, (60m x 0.320 m))

The GC was programmed from 50 to 90°C at a rate of heating of 8°C/min (hold it for 10 min at 90°C) and 90 to 250°C at a rate of heating of 10°C/min (hold it for 5 min at

250°C). The carrier gas used is Helium (He), whereas hydrogen and air are used in the FID detector. Figure (3.3) shows the gas chromatographic (GC) system.

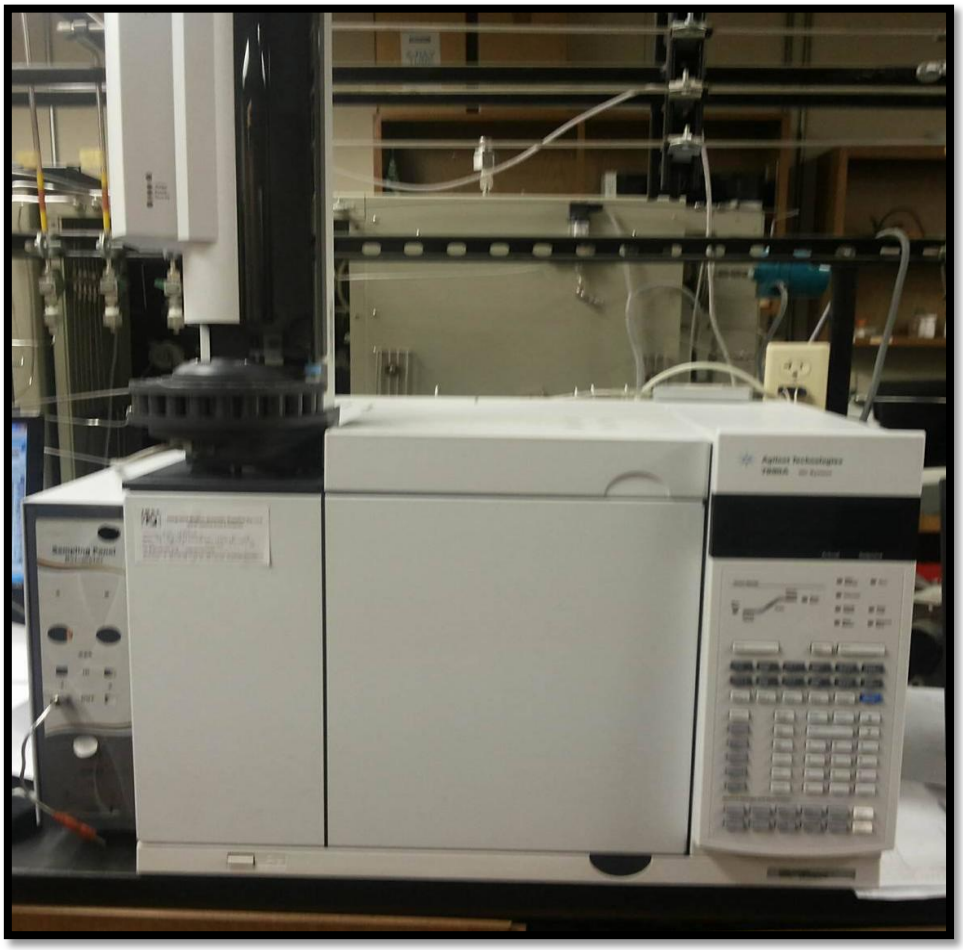


Figure (3.3): Gas Chromatographic (GC) system

3.2 Experimental

3.2.1 Materials

Ammonium metatungstate [$(NH_4)_6H_2W_{12}O_{40}.xH_2O$], molybdenum oxide, molybdenum dioxide bis (acetylacetonate) and SiO_2 nano powder were purchased from Sigma-Aldrich and used without any further purification. 2-pentene was also purchased from Sigma-Aldrich and was further treated with molecular sieves 4A to reduce the moisture. Ethylene gas (99.95 % purity) was purchased from local gas supplier and was passed though columns of molecular sieves and oxygen scavengers to remove the moisture and oxygen.

3.2.2 Support Synthesis

3.2.2.1 Mesoporous MCM-41

Mesoporous support MCM-41 was synthesized by homogeneous precipitation method according to the literature [22]. Hexadecyltrimethyl ammonium bromide (CTABr, Aldrich) was used as a template and sodium silicate (Aldrich) as a silicon source; pH of the synthesis mixture was controlled by the addition of ethyl acetate. The molar composition of the reaction mixture was Na_2SiO_3: CTABr: H_2O: ethyl acetate = 1: 0.33: 644: 1.87

3.2.2.2 Mesoporous SBA-15

Purely siliceous SBA-15 mesoporous molecular sieve was synthesized according to the literature [38] using a "triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$; BASF) as a structure-directing agent.

Tetraethoxysilane (TEOS; 98%, Aldrich) was used as a silica source, yielding a synthesis batch of molar ratio TEOS: HCl: P123: H_2O = 1: 6.2: 0.017: 197. The mixture was stirred at 35°C for 2 minutes and subsequently aged for 24 hours at 35°C and 48 hours at 95°C. The resulting solid was recovered by filtration, extensively washed with distilled water and ethanol, and dried at 95°C overnight.

3.2.2.1 Microporous MCM-22

MCM-22 (NH_4^+ form) was prepared according to the literature [46] using Ludox LS-30 (Aldrich), sodium aluminate (50-55% Al_2O_3, 40-45% Na_2O, Riedel-de-Haen), 50% solution of sodium hydroxide (Aldrich) and hexamethyleneimine (HMI) as a structure-directing agent with the following reactant ratios: Si /Al = 15, OH^-/Si = 0.09, HMI /Si = 0.33 and H_2O /Si = 27. The synthesis gel was loaded into 0.5 L Teflon-lined reactor and the hydrothermal synthesis was carried out at 143 °C for 4 days under agitation (400 rpm) and autogenous pressure (5 bars). Solids were isolated by filtration, washed with water and dried at 60°C. The product, MCM-22P, was calcined under nitrogen at 482°C for 3 hours followed by calcination by using hot air at 540°C (ramp 1°C/min) for 8 hours. Ion-exchange to NH_4-form was performed by four-fold treatment with 1 M NH_4NO_3 solution for 3 hours.

3.2.3 Catalyst Synthesis

Several catalysts were synthesized by supporting molybdenum and tungsten oxide on conventional silica, mesoporous silica SBA-15, MCM-41 and MCM-22 zeolite using thermal spreading and wet impregnation procedures. Loading of 6 wt% of Molybdenum oxide was chosen for our prepared catalyst based on the previous reports [38, 45].

3.2.3.1 Molybdenum containing SiO_2 by thermal spreading method ($MoO_2(acac)_2$ /SiO_2)

The molybdenum oxide catalysts were prepared via the thermal spreading method. Calcined support materials (SiO_2) were carefully mixed with $MoO_2(acac)_2$ by hand-grinding. After that, the physical mixtures were thermally treated at 500°C in a temperature programmed furnace for 8 hours (ramp 1°C /min).

3.2.3.2 Molybdenum containing SiO_2 by thermal spreading method (MoO_3 /SiO_2)

The molybdenum oxide catalysts were prepared via the thermal spreading method. Calcined support materials (SiO_2) were carefully mixed with MoO_3 by hand-grinding. After that, the physical mixtures were thermally treated at 500°C in a temperature programmed furnace for 8 hours (ramp 1°C /min).

3.2.3.3 Molybdenum containing SBA-15 by thermal spreading method ($MoO_2(acac)_2$ /SBA-15)

The molybdenum oxide catalysts were prepared via the thermal spreading method. Calcined support materials (SBA-15) were carefully mixed with $MoO_2(acac)_2$ by hand-grinding. After that, the physical mixtures were thermally treated at 500°C in a temperature programmed furnace for 8 hours (ramp 1°C /min).

3.2.3.4 Molybdenum containing SBA-15 by thermal spreading method (MoO_3 /SBA-15)

The molybdenum oxide catalysts were prepared via the thermal spreading method. Calcined support materials (SBA-15) were carefully mixed with MoO_3 by hand-grinding. After that, the physical mixtures were thermally treated at 500°C in a temperature programmed furnace for 8 hours (ramp 1°C /min).

3.2.3.5 Molybdenum containing MCM-22 by thermal spreading method (MoO_3 /MCM-22)

The molybdenum oxide catalysts were prepared via the thermal spreading method. Calcined support materials (MCM-22) were carefully mixed with MoO_3 by hand-grinding. After that, the physical mixtures were thermally treated at 500°C in a temperature programmed furnace for 8 hours (ramp 1°C /min).

3.2.3.6 Molybdenum containing MCM-41 by thermal spreading method ($MoO_2(acac)_2$ /MCM-41)

The molybdenum oxide catalysts were prepared via the thermal spreading method. Calcined support materials (MCM-41) were carefully mixed with $MoO_2(acac)_2$ by hand-grinding. After that, the physical mixtures were thermally treated at 500°C in a temperature programmed furnace for 8 hours (ramp 1°C /min).

3.2.3.7 Tungsten containing MCM-41 by wet impregnation method (WO_3 /MCM-41)

Catalysts based on tungsten oxide supported on mesoporous molecular sieve were prepared by wet impregnation method according to the literature [39]. Calcined molecular sieves (MCM-41) were carefully mixed with water solution made from ammonium metatungstate [$(NH_4)_6H_2W_{12}O_{40}.xH_2O$] in weight ratios corresponding to catalyst loadings of 6.0 wt. % of W. The aqueous solution of metal oxide was added drop wise to the aqueous slurry of MCM-41 using a small syringe. After that, the mixture was stirred for 3 hours then dried in oven at 80°C for 12 hours and finally calcined at 550°C in a temperature-programmed furnace for 5 hours (ramp 1°C /min).

3.2.3.8 Tungsten containing SBA-15 by wet impregnation method (WO_3/SBA-15):

Catalysts based on tungsten oxide supported on mesoporous molecular sieve were prepared by wet impregnation method according to the literature [39]. Calcined molecular sieves (SBA-15) were carefully mixed with water solution made from ammonium metatungstate [$(NH_4)_6H_2W_{12}O_{40}.xH_2O$] in weight ratios corresponding to catalyst loadings of 6.0 wt. % of W. The aqueous solution of metal oxide was added drop wise to the aqueous slurry of SBA-15 using a small syringe. After that, the mixture was stirred for 3 hours then dried in oven at 80°C for 12 hours and finally calcined at 550°C in a temperature-programmed furnace for 5 hours (ramp 1°C /min).

Table (3.1): All prepared catalyst with metal loading and Si /Al ratio

Catalyst	**Metal Loading (wt.%)**	**Si /Al ratio**
$MoO_2(acac)_2$ /SiO_2	6	All Silica
MoO_3 /SiO_2	6	All Silica
$MoO_2(acac)_2$ /SBA-15	6	All Silica
MoO_3 /SBA-15	6	All Silica
WO_3 /SBA-15	6	All Silica
WO_3 /MCM-41	6	All Silica
$MoO_2(acac)_2$ / MCM-41	6	All Silica
MoO_3 /MCM-22	6	15

3.2.4 Catalyst Characterization

3.2.4.1 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) data were obtained on a Bruker AXS D8 Advance diffractometer with a graphite monochromator and a Vantec-1 position sensitive detector using Cu Kα radiation (at 40 kV and 30 mA) in Bragg−Brentano geometry.

3.2.4.2 Nitrogen adsorption/desorption isotherms

Nitrogen adsorption/desorption isotherms were measured on a "Micromeritics ASAP 2020 at liquid nitrogen temperature (−196°C) to determine the BET area and pore volume. Prior to the sorption measurements, all samples were degassed on a Micromeritics Flow-Prep060 instrument under helium at 110°C for 6 hours.

3.2.4.3 ICP-OES

The Mo and W contents in catalysts were analyzed by ICP-OES (Thermo Scientific iCAP 7000 Series). The samples were mineralized using a mixture of HCl, HNO_3 and HF in a microwave oven.

3.3 GC Calibration

To determine the product distribution and composition that produced from C_5 reactions over different catalyst we should first do the gas chromatograph calibration

3.3.1 Retention time determination for all compounds

The retention times of all compounds of interest in this work were determined by analyzing pure samples of each of the compounds in the GC on both FID. Table 3.2 shows the different hydrocarbons and their corresponding retention times on FID2 B and Table 3.3 shows the different aromatics retention times on FID1 A. These retention times were used to identify each component of the reaction products.

Table (3.2): Paraffins & Olefins Retention time in the GC FID2 B

Compounds	Retention Time (min)
Methane	3.90
Ethane	4.88
Ethylene	5.39
Propane	7.92
Propylene	11.07
Iso-butane	12.65
n-Butane	13.54
1-Butene	17.13
trans-2-Butene	18.25
Iso-Butylene	18.40
Cis-2-Butene	18.62
Iso-Pentane	18.83
n-Pentane	19.56
3-Me-1-butene	21.80
1-Pentene	22.40
trans-2-Pentene	23.30
cis-2-Pentene	23.75
2 Methyl-2 Butene	24.65
4-Me-1-Pentene	27.61
1-Hexene	28.11
trans-3-Hexene	28.65
trans-2-Hexene	29.00
cis-3-hexene	29.10
2-Methyl-2-Pentene	29.20

Cis-2-Hexene	29.49
trans-2-Methyl-3-Hexene	29.99
cis-2-Methyl-3-Hexene	32.41
1-Heptene	32.71
trans-3-Heptene	32.95
cis-3-Heptene	33.11
cis-3-Methyl-3-Hexene	33.22
trans-2-Heptene	33.26
cis-2-Heptene	33.47
1-Octene	35.69
3,4-Dimethyl-3-Hexene	35.81
trans-2-Octene	35.98
cis-2-Octene	36.29
1-Nonene	38.44
trans-3-Nonene	38.61
cis-3-Nonene	38.91
trans-2-Nonene	39.11
cis-2-Nonene	39.60
1-Decene	41.90

Table (3.3): Aromatics Retention time in the GC on FID1 A

Compounds	Retention Time (min)
Benzene	7.68
Toluene	10.11
Ethylbenzene	12.48
m-Xylene	12.64
p-Xylene	12.91
o-Xylene	14.20
i-Propyl benzene	15.07
n-Propyl benzene	15.52

3.4 Catalysts Evaluation

3.4.1 Testing Procedure

The metathesis reaction of 2-pentene (a mixture of cis-2-pentene & trans-2-pentene) was did in a fixed-bed tubular reactor (stainless steel tube grade 316 material , 5.16 mm ID × 9.53 mm OD × 200 mm length). In a typical experiment, the reactor was charged with 0.5 ml of catalyst previously sieved to a particle size of 0.5-1.0 mm diameter. The catalyst sample was first activated in a nitrogen stream at 550°C for 1 hour. The flow rates of feed (2-pentene) and N_2 were maintained at 0.05 ml/min and 10 ml/min, respectively, during the reaction. The metathesis reaction was carried out at different temperatures, ranging from 200 to 500°C, 5-12 hours time-on-stream (TOS) and atmospheric pressure. The quantitative analysis of the reaction products was carried out using an on-line Agilent GC equipped with FID detectors using GS-Gaspro and Innowax columns.

3.4.2 Metathesis Experiment

A systematic study of metathesis reactions of 2-pentene was performed over molybdenum and tungsten oxide supported on conventional silica, mesoporous molecular sieves (SBA-15 and MCM-41) and MCM-22 zeolite. 2-pentene can undergo a series of different reactions as presented in Figure 3.4 including:

i) Isomerization (both double bond shift and skeletal) to produce 1-$C_5^=$ (1-pentene), 2-Me-2-$C_4^=$ (2-methyl-2-butene), 2-Me-1-$C_4^=$ (2-methyl-1-butene) and 3-Me-1-$C_4^=$ (3-methyl-1-butene) isomers.

ii) Cracking reaction to produce $C_2^=$ (ethylene) and $C_3^=$ (propylene), which can further undergo oligomerization/aromatization to produce higher olefins or aromatics.

iii) Self-metathesis (i.e. with another molecule of 2-$C_5^=$) to produce 2-$C_4^=$ (2-butene) and 3-$C_6^=$ (3-hexene).

iv) Cross-metathesis with any other molecule of olefin present in the reaction mixture (Figure 3.4).

The conversion of 2-pentene and the selectivity of products were calculated using following equations (3.1 & 3.2):

$$\text{Conversion of 2-}C_5^= = 100 \times \frac{\text{Amount of 2-}C_5^= \text{ in feed} - \text{Amount of 2-}C_5^= \text{ in product}}{\text{Amount of 2-}C_5^= \text{ in feed}} \quad (3.1)$$

$$\text{Selectivity of product } i \text{ (\%)} = 100 \times \frac{\text{Amount of product } i}{\text{Sum of amounts of all products}} \quad (3.2)$$

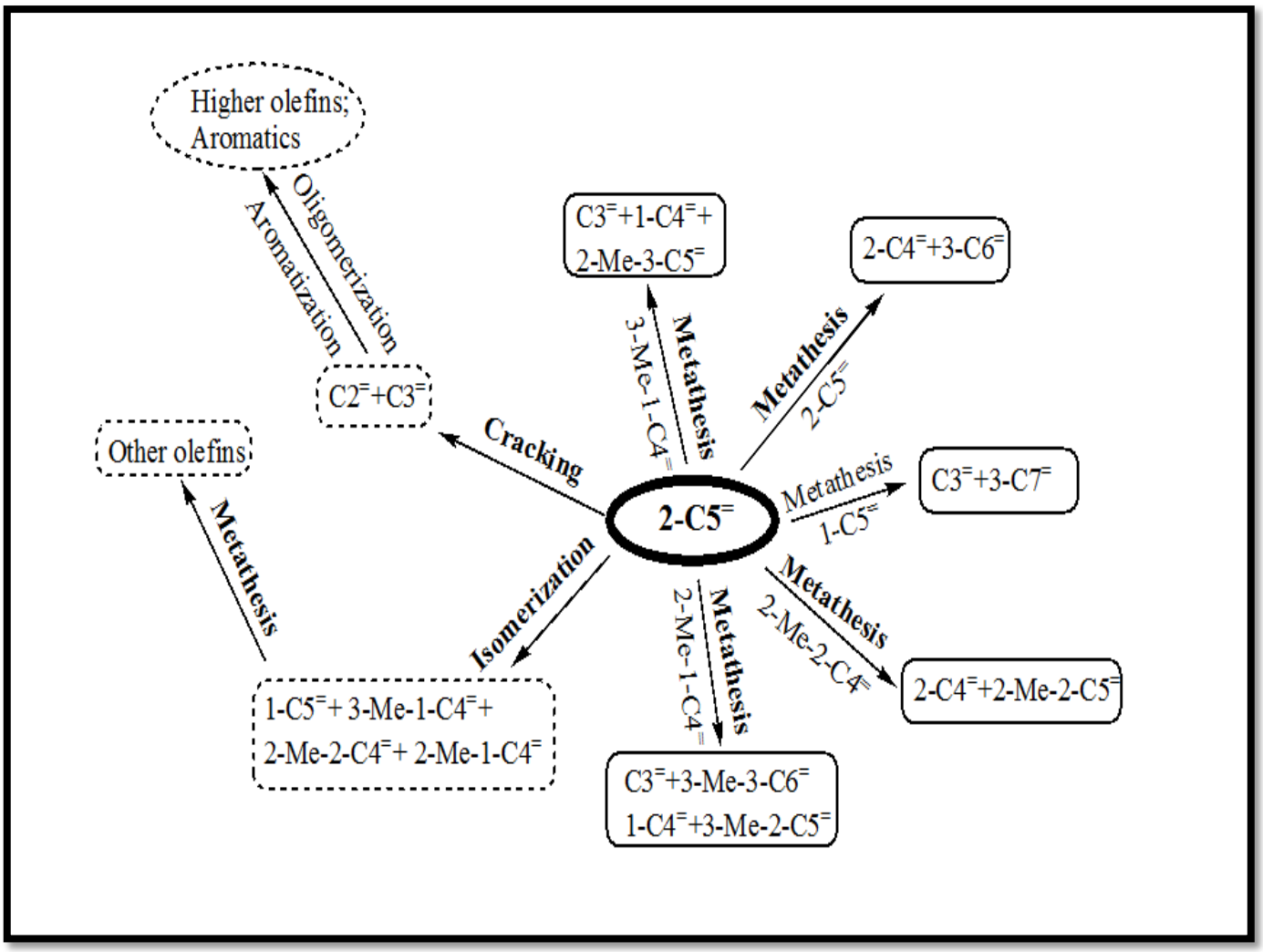


Figure (3.4): Different possible reactions during conversion of 2-$C_5^=$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

All catalysts and supports were characterized by X-ray powder diffraction (XRD). Diffraction patterns proved that (i) the structure of supports is preserved in the catalysts (ii) the catalysts do not contain crystalline MoO_3 and WO_3. Figure (4.1) shows X-ray powder diffraction patterns of catalyst MoO_3 /MCM-22 and of parent support MCM-22. Both XRD patterns are practically identical no diffraction lines of MoO_3 crystallites in catalysts (at 2θ = 12.7°, 23.3°, 25.7° and 27.3° [38, 47]) are visible. It suggests good dispersion of MoO_x species on the surface which is a prerequisite for a catalyst good activity in metathesis [38]. Similarly, the agreement between XRD patterns of mesoporous sieve based catalysts and corresponding supports indicates a preservation of sieves architecture, Figure (4.2). The absence of MoO_3 and WO_3 signals (2θ = 23.1°, 23.6°, and 24.4° [48]) was observed in the region 10-30° (not shown in Figure 4.2).

Textural parameters determined from N_2 isotherms show a decrease in surface area BET (S_{BET}) values after the modification of the parent support with Mo or W oxides [38, 45]. Only a small reduction in pore size was observed while the mesoporous character of all catalysts base on mesoporous molecular sieves was preserved, Table (4.1) shows more details.

Catalyst loading determined by chemical analysis using an ICP-OES spectrometer was the same as that one calculated from the amount of metal oxide used for catalyst preparation.

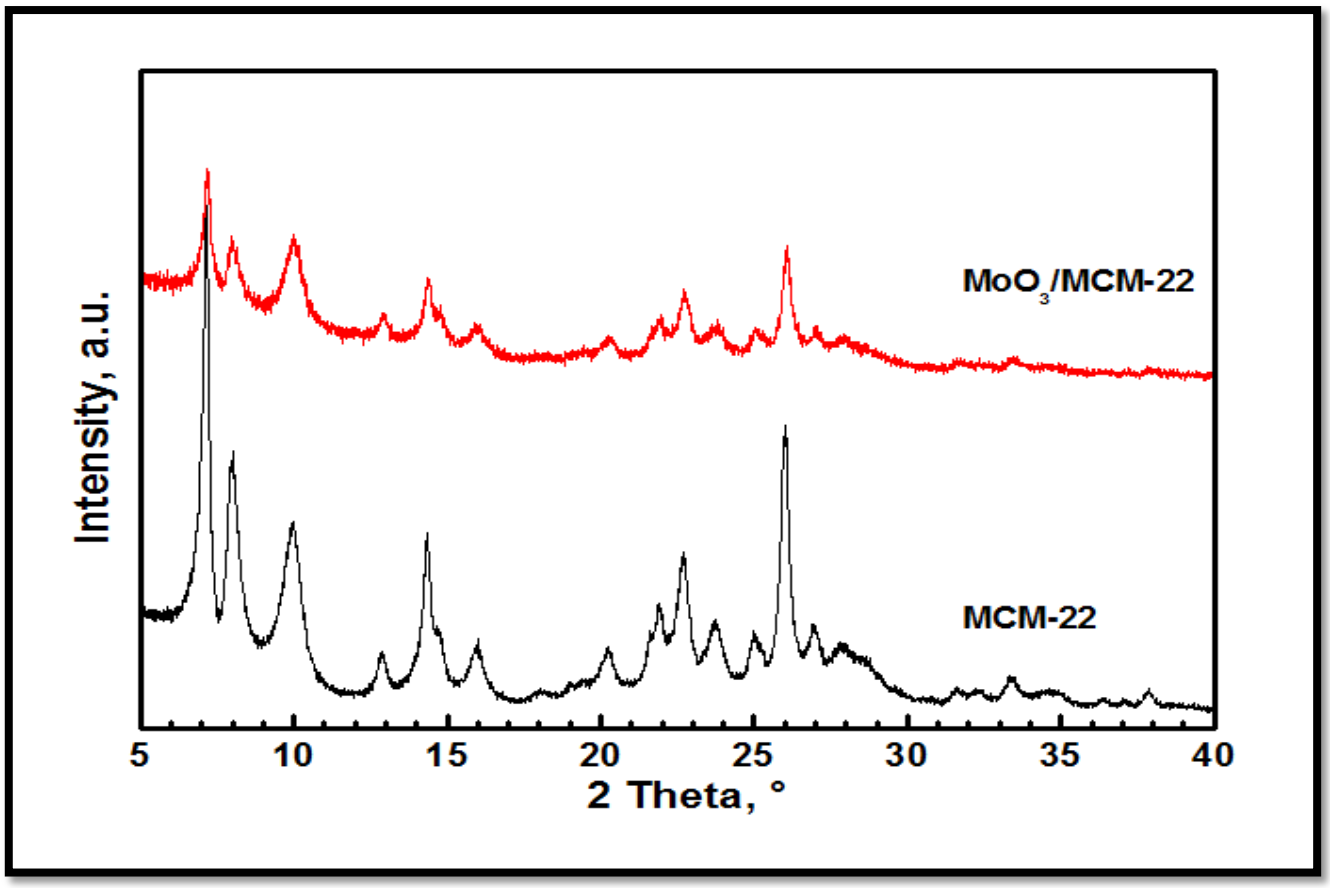


Figure (4.1): XRD patterns of catalyst MoO_3 /MCM-22 and of its parent support.

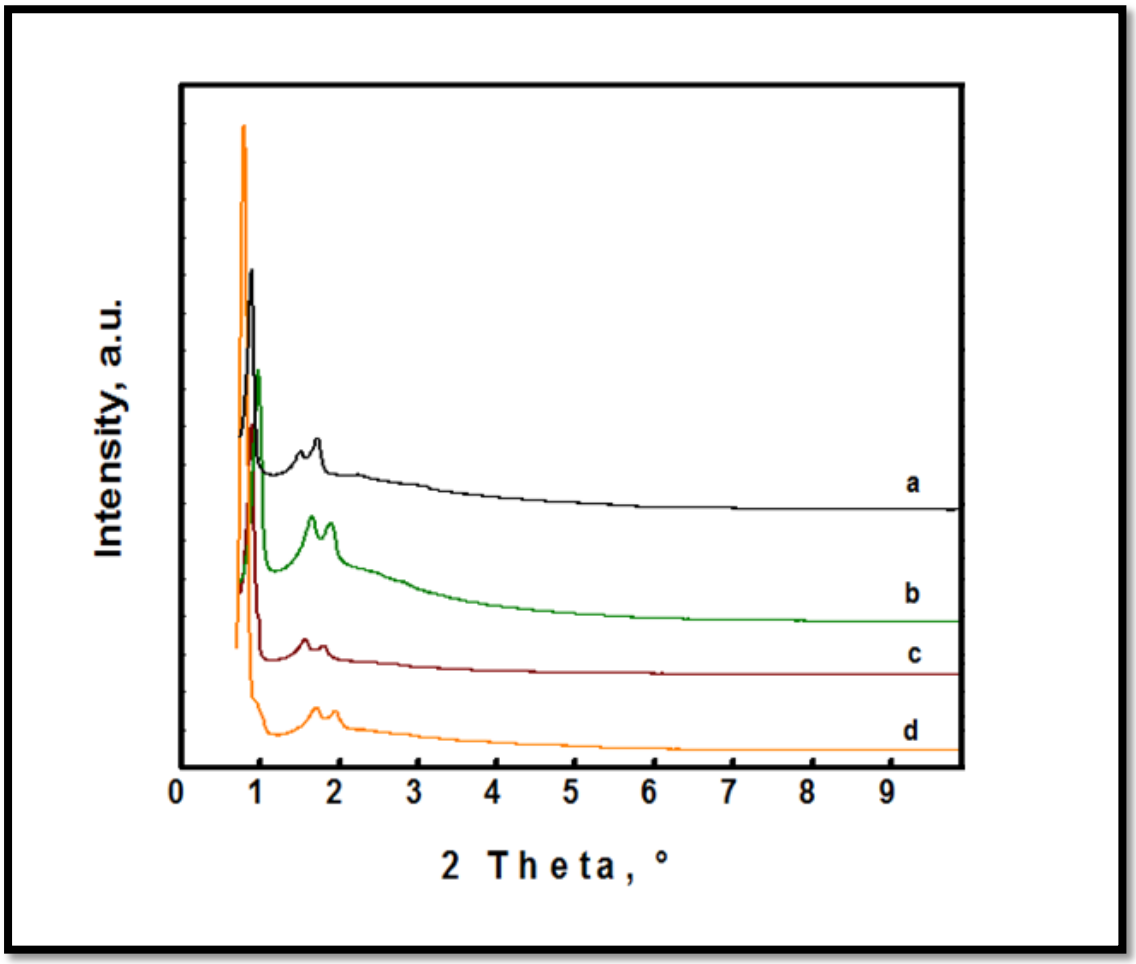


Figure (4.2): XRD patterns for catalysts on SBA-15

(Parent SBA-15 (a), WO_3 /SBA-15 (b), $MoO_2(acac)_2$ /SBA-15 (c), MoO_3 /SBA-15 (d))

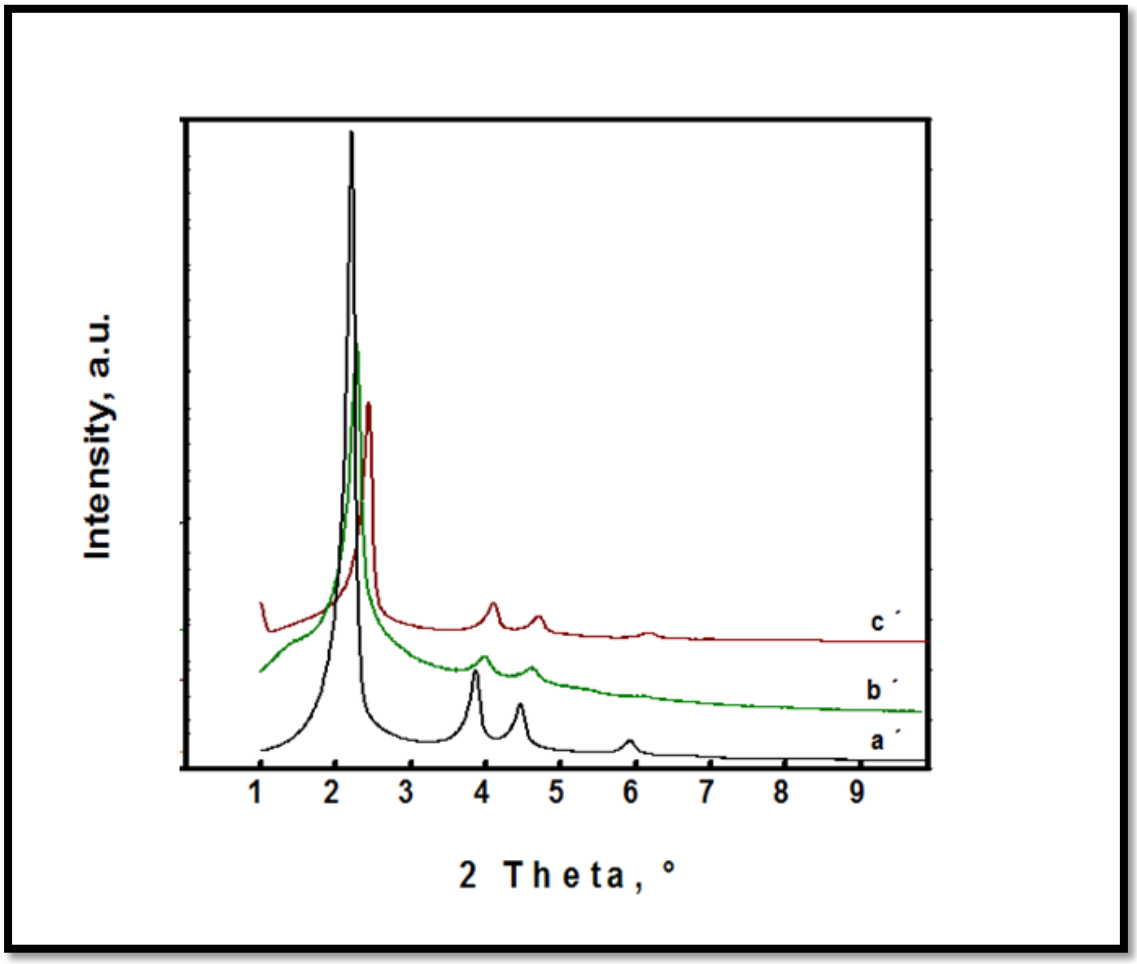


Figure (4.3): XRD patterns for catalysts on MCM-41

(Parent MCM-41 (a´), WO_3 /MCM-41 (b´), $MoO_2(acac)_2$ /MCM-41 (c´))

Table (4.1): The catalysts and supports Sorption characteristics obtained from nitrogen adsorption isotherms.

Sr. #	Catalysts	S_{BET} (m^2/g)	d (nm)	V_{TOT} (cm^3/g)	S_{ext} (m^2/g)
1	SiO_2	69	-	0.16	56
2	MoO_3 /SiO_2	43	-	0.05	38
3	$MoO_2(acac)_2$ /SiO_2	49	-	0.06	44
4	MCM-22	455	-	0.59	120
5	MoO_3 /MCM-22	423	-	0.38	119
6	MCM-41	1040	3.9	0.86	1023
7	$MoO_2(acac)_2$ /MCM-41	1006	3.7	0.79	1000
8	SBA-15	877	6.4	1.07	666
9	$MoO_2(acac)_2$ /SBA-15	733	5.7	0.98	594
10	MoO_3 /SBA-15	719	5.5	0.88	540
11	WO_3 /SBA15	639	5.1	0.86	531
12	WO_3 /MCM-41	614	3.5	0.36	571

S_{BET} = surface area (BET method, $p/p_0 = 0.05 – 0.20$)
V_{TOT} = total pore volume (at $p/p_0 = 0.95$)
$S_{ext} = S_{BET} - S_{MICRO}$ (from t-plot)
D = average pore diameter (NLDFT, N_2 on oxides at 77 K, cylindrical pores)

4.2 Metathesis of 2-Pentene

4.2.1 Catalysts Activity and Conversion

The results of metathesis reaction of 2-pentene at 500°C under atmospheric pressure over different catalysts is presented in (Tables (4.2)-(4.9)) and (Figure (4.4)). The MoO_3 /MCM-22 exhibited the highest conversion of 2-$C_5^=$ (79%) whereas with MoO_3 /SiO_2 the lowest conversion was achieved (8%). The product distribution revealed that molybdenum supported on conventional silica exhibited only isomerization reaction of 2-pentene mainly to 1-pentene. MoO_3 /MCM-22 catalyzed 2-pentene isomerization, metathesis and cracking reactions resulting in the highest amounts of ethylene and propylene produced as compared to other catalysts. It also resulted in the formation of C_4 and C_5 paraffins due to hydrogen transfer reactions. In contrast to catalysts supported by SiO_2, the isomerization of 2-pentene led to high amounts of 2-methyl-2-butene (20.9 %) as a result of skeletal isomerization induced by Brønsted acid sites of zeolite support. The close inspection of butene isomers revealed the maximum amount of i-butene (8%) as compared to other catalysts. The metathesis reaction of 2-pentene produced 2-butene which undergo similar skeletal isomerization to isobutene. Similarly in case of hexenes linear as well as branched isomers of hexene were observed due to skeletal isomerization induced by Brønsted acid sites of zeolite support.

Table (4.2): Product distribution (mole %) of 2-pentene metathesis at 500ºC under atmospheric pressure after stream time of 2 hour over MoO_3 /SiO_2 catalyst

Component name	Yield (mol %)
2-$C_5^=$ Conversion	8.3
C_1	0
C_2	0
$C_2^=$	0
C_3	0
$C_3^=$	0
i-C_4	0
n-C_4	0
1-$C_4^=$	0
t-2-$C_4^=$	0
i-$C_4^=$	0
c-2-$C_4^=$	0
i-C_5	0
n-C_5	0
3-Me-1-$C_4^=$	0
1-$C_5^=$	7.1
t-2-$C_5^=$	62.4
c-2-$C_5^=$	29.3
2-Me-2-$C_4^=$	1.2
$C_6^=$	0
$C_7^=$	0
$C_8^=$	0
$C_9^=$+	0
Aromatics	0

Table (4.3): Product distribution (mole %) of 2-pentene metathesis at 500ºC under atmospheric pressure after stream time of 2 hour over $MoO_2(acac)_2/SiO_2$ catalyst

Component name	Yield (mol %)
2-$C_5^=$ Conversion	10.8
C_1	0
C_2	0
$C_2^=$	0
C_3	0
$C_3^=$	0
i-C_4	0
n-C_4	0
1-$C_4^=$	0
t-2-$C_4^=$	0
i-$C_4^=$	0
c-2-$C_4^=$	0
i-C_5	0
n-C_5	0
3-Me-1-$C_4^=$	0
1-$C_5^=$	9.2
t-2-$C_5^=$	60.3
c-2-$C_5^=$	28.8
2-Me-2-$C_4^=$	1.7
$C_6^=$	0
$C_7^=$	0
$C_8^=$	0
$C_9^=$+	0
Aromatics	0

Table (4.4): Product distribution (mole %) of 2-pentene metathesis at 500ºC under atmospheric pressure after stream time of 2 hour over MoO_3 /MCM-22 catalyst

Component name	Yield (mol %)
2-$C_5^=$ Conversion	78.7
C_1	0
C_2	0
$C_2^=$	6.7
C_3	1.4
$C_3^=$	14.7
i-C_4	1.2
n-C_4	0.8
1-$C_4^=$	2.5
t-2-$C_4^=$	4.2
i-$C_4^=$	8.1
c-2-$C_4^=$	2.8
i-C_5	1.5
n-C_5	2.5
3-Me-1-$C_4^=$	1.7
1-$C_5^=$	2.3
t-2-$C_5^=$	7.8
c-2-$C_5^=$	13.5
2-Me-2-$C_4^=$	20.9
$C_6^=$	3.7
$C_7^=$	1.8
$C_8^=$	0.6
$C_9^=$+	0.3
Aromatics	1

Table (4.5): Product distribution (mole %) of 2-pentene metathesis at 500ºC under atmospheric pressure after stream time of 2 hour over MoO_3 /SBA-15 catalyst

Component name	Yield (mol %)
2-$C_5^=$ Conversion	39.1
C_1	0.5
C_2	0
$C_2^=$	0.8
C_3	0
$C_3^=$	5
i-C_4	0
n-C_4	0
1-$C_4^=$	3.8
t-2-$C_4^=$	4.5
i-$C_4^=$	0
c-2-$C_4^=$	3.2
i-C_5	0
n-C_5	0.3
3-Me-1-$C_4^=$	0
1-$C_5^=$	9.2
t-2-$C_5^=$	40.1
c-2-$C_5^=$	20.8
2-Me-2-$C_4^=$	1.7
$C_6^=$	6.4
$C_7^=$	2.5
$C_8^=$	0.8
$C_9^=$+	0
Aromatics	0.3

Table (4.6): Product distribution (mole %) of 2-pentene metathesis at 500ºC under atmospheric pressure after stream time of 2 hour over $MoO_2(acac)_2$ /SBA-15 catalyst

Component name	Yield (mol %)
2-$C_5^=$ Conversion	41.5
C_1	0
C_2	0
$C_2^=$	0.8
C_3	0
$C_3^=$	5.2
i-C_4	0
n-C_4	0
1-$C_4^=$	3.6
t-2-$C_4^=$	4.3
i-$C_4^=$	0
c-2-$C_4^=$	3.2
i-C_5	0
n-C_5	0
3-Me-1-$C_4^=$	0
1-$C_5^=$	11.4
t-2-$C_5^=$	37.2
c-2-$C_5^=$	21.2
2-Me-2-$C_4^=$	3.1
$C_6^=$	7.1
$C_7^=$	2.6
$C_8^=$	0.3
$C_9^=$+	0
Aromatics	0

Table (4.7): Product distribution (mole %) of 2-pentene metathesis at 500ºC under atmospheric pressure after stream time of 2 hour over $MoO_2(acac)_2$ /MCM-41 catalyst

Component name	Yield (mol %)
2-$C_5^=$ Conversion	50
C_1	0.3
C_2	0
$C_2^=$	1.3
C_3	0
$C_3^=$	7.6
i-C_4	0
n-C_4	0
1-$C_4^=$	4.7
t-2-$C_4^=$	6
i-$C_4^=$	0
c-2-$C_4^=$	4.3
i-C_5	0
n-C_5	0.4
3-Me-1-$C_4^=$	0
1-$C_5^=$	8.9
t-2-$C_5^=$	32.4
c-2-$C_5^=$	17.5
2-Me-2-$C_4^=$	1.6
$C_6^=$	8.8
$C_7^=$	4.4
$C_8^=$	1.6
$C_9^=$+	0.3
Aromatics	0.2

Table (4.8): Product distribution (mole %) of 2-pentene metathesis at 500ºC under atmospheric pressure after stream time of 2 hour over WO_3/SBA-15 catalyst

Component name	Yield (mol %)
2-$C_5^=$ Conversion	56.5
C_1	0
C_2	0
$C_2^=$	1.1
C_3	0
$C_3^=$	8.9
i-C_4	0
n-C_4	0
1-$C_4^=$	5.6
t-2-$C_4^=$	6.9
i-$C_4^=$	0.8
c-2-$C_4^=$	5.1
i-C_5	0
n-C_5	0
3-Me-1-$C_4^=$	0
1-$C_5^=$	5.8
t-2-$C_5^=$	27.8
c-2-$C_5^=$	15.8
2-Me-2-$C_4^=$	2.6
$C_6^=$	11.6
$C_7^=$	5
$C_8^=$	1.8
$C_9^=$+	0.5
Aromatics	1.0

Table (4.9): Product distribution (mole %) of 2-pentene metathesis at 500ºC under atmospheric pressure after stream time of 2 hour over WO_3/MCM-41 catalyst

Component name	Yield (mol %)
2-$C_5^=$ Conversion	67.9
C_1	0.0
C_2	0.0
$C_2^=$	1.4
C_3	0.0
$C_3^=$	12.7
i-C_4	0.0
n-C_4	0.0
1-$C_4^=$	6.2
t-2-$C_4^=$	8.6
i-$C_4^=$	0.9
c-2-$C_4^=$	6.4
i-C_5	0.0
n-C_5	0.0
3-Me-1-$C_4^=$	0.0
1-$C_5^=$	5.7
t-2-$C_5^=$	18.9
c-2-$C_5^=$	13.3
2-Me-2-$C_4^=$	6.6
$C_6^=$	12.8
$C_7^=$	5.2
$C_8^=$	1.3
$C_9^=$+	0
Aromatics	0

Catalysts based on mesoporous molecular sieves initiated metathesis reaction of 2-pentene as a dominant reaction. Therefore propylene, C_4 olefins and $C_{6+}^{=}$ were observed as major products. The self-metathesis reaction of 2-pentene resulted in the formation of 2-butene and 3-hexene, whereas cross-metathesis between 2-pentene and 1-pentene (produced from isomerization of 2-$C_5^{=}$) resulted in the creation of propylene and 3-heptene. The product distribution revealed that among C_4 olefins, only 2-butene (cis & trans) and 1-butenes were present, whereas i-butene was absent. The higher amount of 2-butene indicated that it was produced from self-metathesis reaction of 2-pentene and then underwent double bond isomerization to produce 1-butene. Similarly in the case of $C_6^{=}$ isomers, only 1-hexene, 2-hexene (trans & cis) and 3-hexene (trans & cis) were observed over these catalysts. 3-hexene was observed in larger concentration as compared to that of 1 & 2-hexenes. Therefore it can be concluded that these catalysts can cause double bond isomerization to produce linear isomers of olefins but cannot cause skeletal isomerization to produce branched isomers of olefins.

The 2-pentene conversion increased in the following order of catalysts used MoO_3 /SBA-15 < $MoO_2(acac)_2$ /SBA-15 < $MoO_2(acac)_2$ /MCM-41 < WO_3 /SBA-15 < WO_3 /MCM-41. It was interesting to note that over both Mo and W oxides supported on MCM-41 higher conversions were reached than over catalysts based on SBA-15 in spite of larger pore diameter of SBA-15 which was supposed to favor the diffusion of substrate and reaction products. A similar trend has been reported by Topka et al. [38] during metathesis of 1-octene. MoO_3 /MCM-41 exhibited higher metathesis activity for 1-octene as compared to that of MoO_3 /SBA-15 because of imperfect dispersion of Mo oxide on SBA-15 surface (manifested by the presence of high fractions of inactive bulk MoO_3 and low active polymolybdate species) [23].

In another study [39], a similar observation was reported during metathesis of 2-butene over WO_3-SBA-15 & WO_3-MCM-41. The WO_3-MCM-41 exhibited higher metathesis activity than that of WO_3-SBA-15. The higher activity was explained based on the well-dispersed WO_3 species over MCM-41 as compared to that of SBA-15.

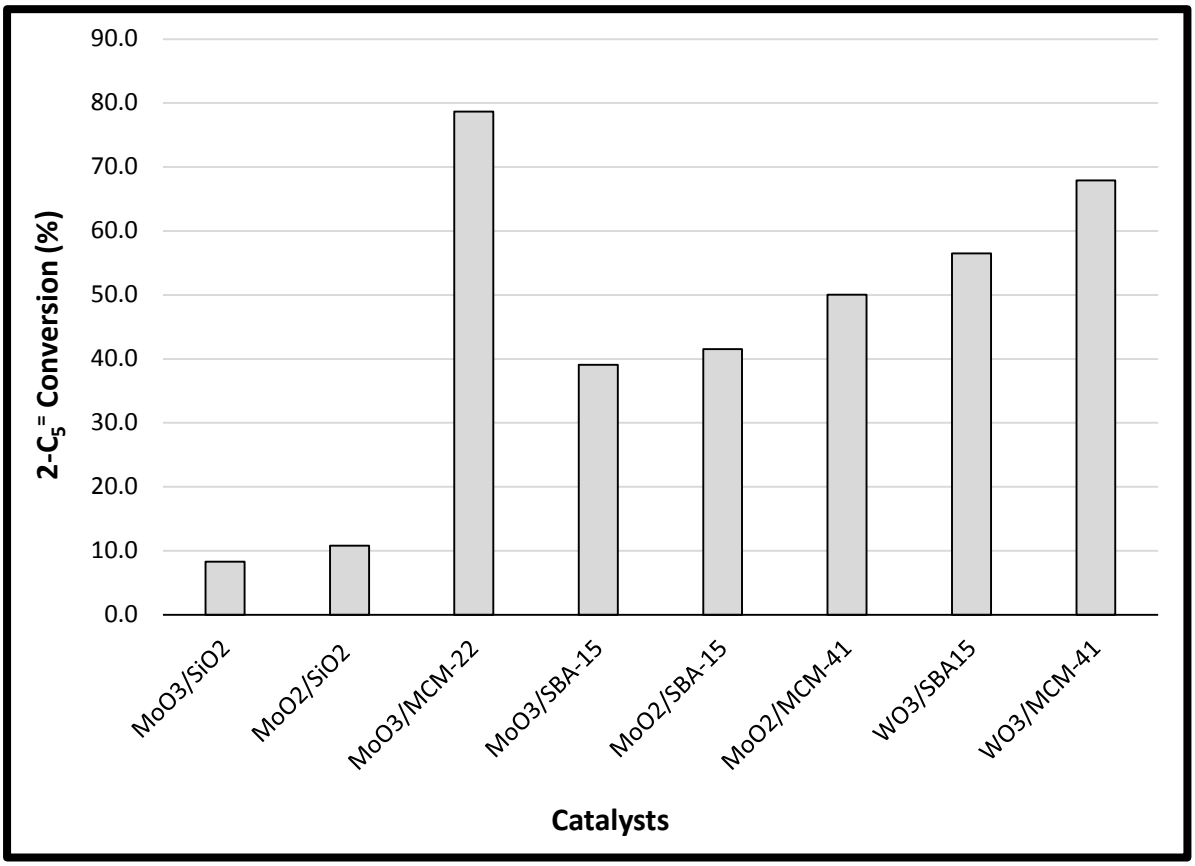


Figure (4.4): Conversion of 2-pentene over different catalysts at 500°C and atmospheric pressure.

4.2.2 Effect of Reaction Temperature

Metathesis of 2-pentene over MoO_3 /MCM-22, $MoO_2(acac)_2$ /SBA-15, $MoO_2(acac)_2$ /MCM-41, WO_3 /SBA-15, and WO_3 /MCM-41 was carried out under different reaction temperatures ranging from 200 to 500°C (according to the literature W and Mo based catalysts require high temperature from 200 to 500°C). The compositions of the grouped products are plotted against the reaction temperature in tables (4.10) - (4.14) & figures (4.5) - (4.9).

In the case of MoO_3 /MCM-22, only $C_5^=$ isomerization products were observed from 200 to 300°C. However ethylene, propylene, butenes, $C_{6+}^=$, paraffins and aromatics (indicating metathesis and cracking reactions) appeared at 350°C and their amount (0.0, 1.7, 12.0, 9.3, 3.8 & 0 % respectively) increased with increasing temperature till 500 °C (6.7, 14.7, 17.6, 6.2, 7.4 & 1.0 % respectively).

Table (4.10): The products composition as a function of temperature for 2-pentene reaction over MoO_3 /MCM-22

Yield (%)	Temperature (°C)					
	200	**250**	**300**	**350**	**400**	**500**
Conversion	9.601	16.107	18.160	64.423	76.934	78.687
Ethylene					0.995	6.700
Propylene				1.735	9.171	14.697
Butenes		0.671	0.778	12.012	16.752	17.642
C_5 Isomers	9.601	15.436	16.981	40.550	31.522	24.900
C_5 Feed	90.399	83.893	81.840	32.577	23.066	21.313
C_6^+			0.401	9.313	10.182	6.4
Parafins				3.814	7.705	7.394
Aromatics					0.616	0.987
Total	100.000	100.000	100.000	100.000	100.000	100.000

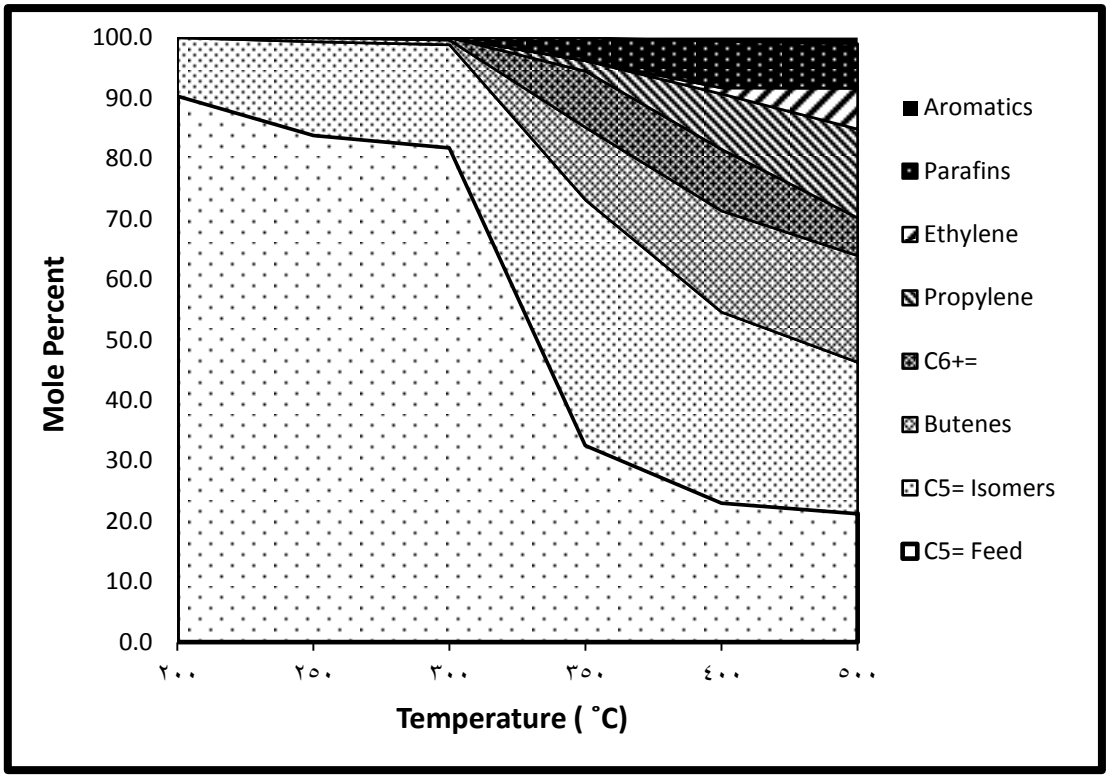


Figure (4.5): Variation in the products composition as a function of temperature for 2-pentene reaction over MoO_3 /MCM-22

In the case of $MoO_2(acac)_2$/MCM-41 only $C_5^=$ isomerization products were observed from 200 to 250°C. However Ethylene, propylene, butenes and $C_{6+}^=$ (0.0, 0.4, 1.2 & 1.2) % respectively, indicating self-metathesis between two molecules of 2-pentene and cross-metathesis between 2-pentene and 1-pentene molecules) also appeared in the product mixtures at 300°C and their amount further increased (1.3, 7.6, 15.0 & 15.0 respectively) till 500°C.

Table (4.11): The products composition as a function of temperature for 2-pentene reaction over $MoO_2(acac)_2$ /MCM-41

Yield (%)	Temperature (ºC)						
	200	**250**	**300**	**350**	**400**	**450**	**500**
Conversion	5.905	7.813	15.099	24.679	39.039	44.485	50.000
Ethylene	0.000				0.300	0.510	1.310
Propylene	0.000		0.400	1.500	4.385	5.677	7.560
Butenes	0.000		1.239	4.094	10.583	12.911	14.990
C_5 Isomers	5.637	7.551	12.213	14.735	12.269	10.795	10.584
C_5 Feed	94.095	92.187	84.901	75.321	60.961	55.514	49.982
C_6^+			1.243	4.340	11.124	14.330	15.040
Aromatics						0.100	0.170
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000

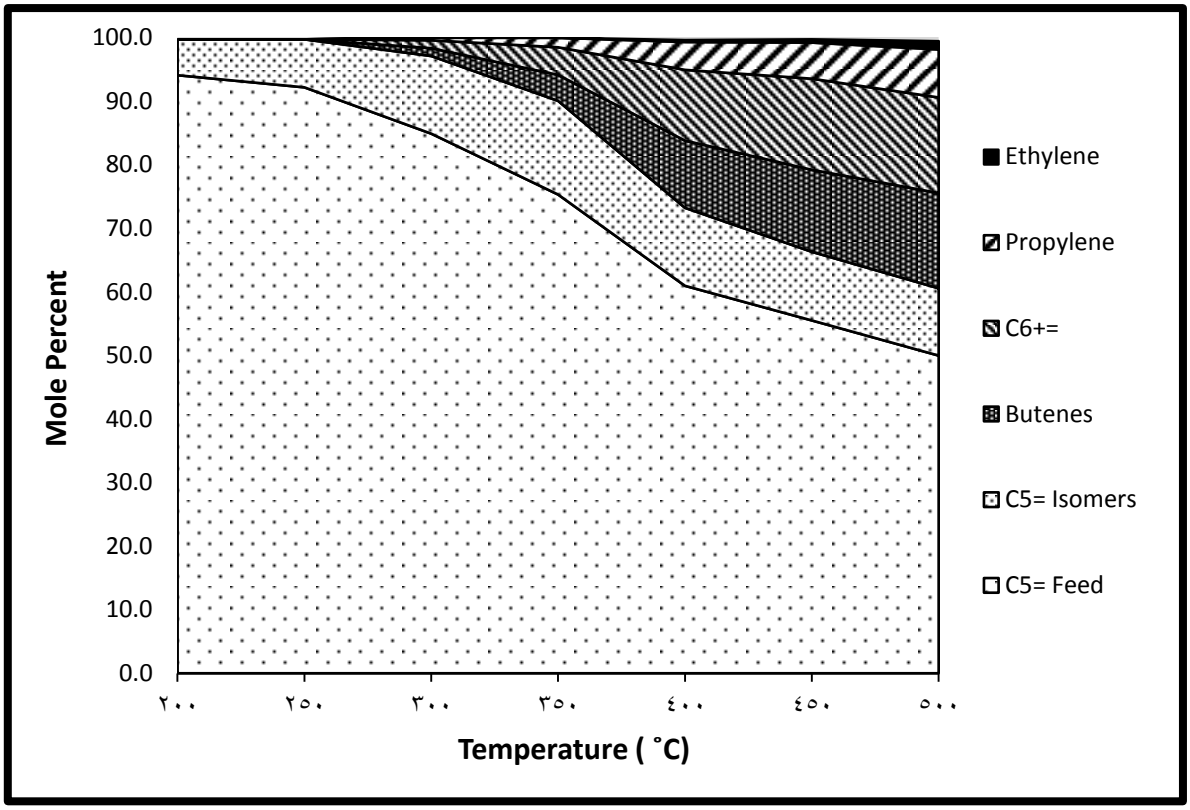


Figure (4.6): Variation in the products composition as a function of temperature for 2-pentene reaction over $MoO_2(acac)_2$ /MCM-41.

In the case of $MoO_2(acac)_2$/SBA-15 only $C_5^=$ isomerization products were observed from 200 to 300°C and metathesis products i.e. ethylene, propylene, butenes and $C_{6+}^=$ (0.0, 1.2, 4.2 & 4.6 % respectively) also appeared in the product mixtures at 350°C and their amount further increased (0.8, 5.2, 11.0 & 10.0 % respectively) till 500°C.

Table (4.12): The products composition as a function of temperature for 2-pentene reaction over $MoO_2(acac)_2$ /SBA-15

Yield (%)	Temperature (°C)						
	200	**250**	**300**	**350**	**400**	**450**	**500**
Conversion	2.500	5.300	11.500	18.000	29.020	40.417	41.540
Ethylene					0	0.545	0.810
Propylene			0.600	1.205	2.700	4.200	5.170
Butenes			1.900	4.214	8.400	10.577	11.040
C_5 Isomers	2.500	5.300	7.800	8.000	8.200	11.859	14.560
C_5 Feed	97.500	94.700	88.500	82.000	70.980	59.583	58.460
C_6^+			1.200	4.581	9.700	13.409	9.980
Aromatics			0.000		0.000	0.000	0.000
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000

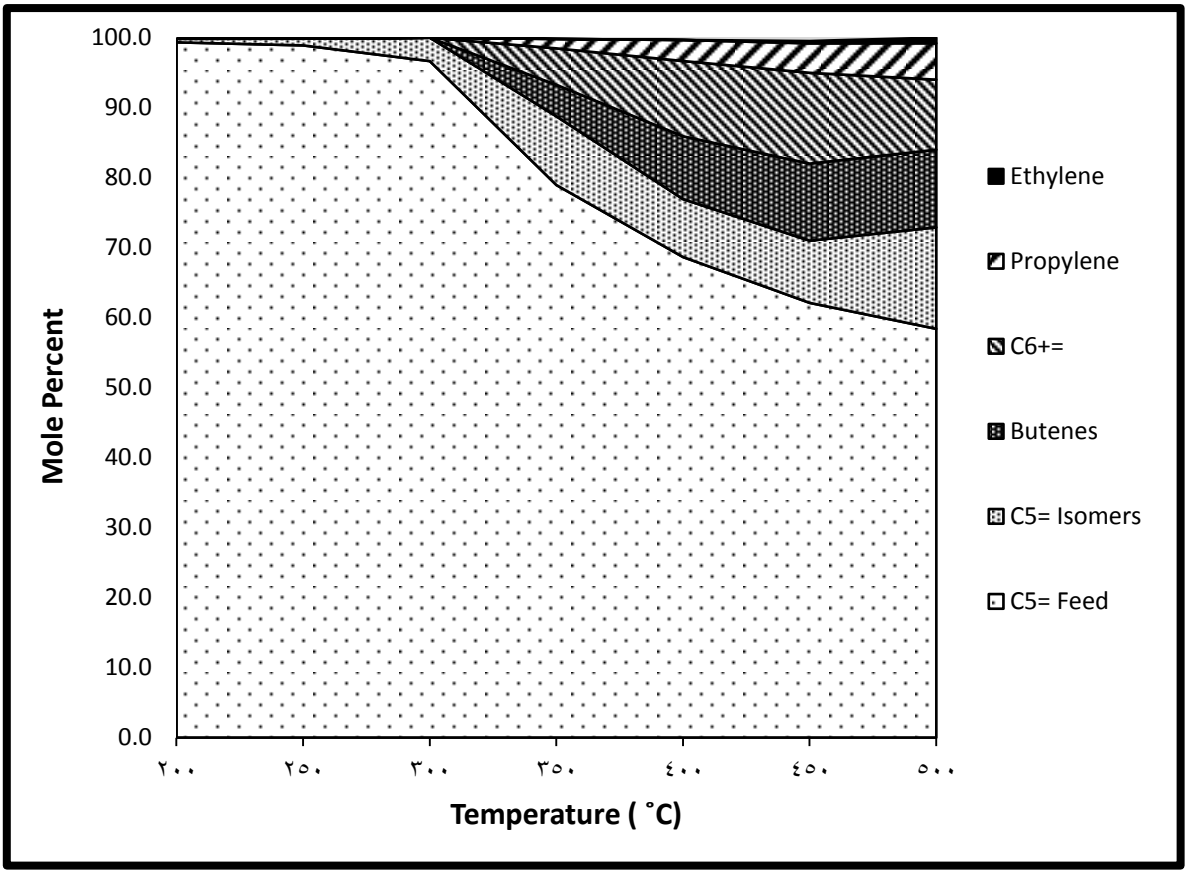


Figure (4.7): Variation in the products composition as a function of temperature for 2-pentene reaction over $MoO_2(acac)_2$ /SBA-15.

In the case of WO_3 /MCM-41 only $C_5^=$ isomerization products were observed from 200 to 350°C and metathesis products ethylene, propylene, butenes and $C_{6+}^=$ (0.0, 0.7, 2.0 & 1.7 % respectively) appeared in the product mixtures at 400°C and their amount further increased (1.4, 12.7, 22.1 & 19.3 % respectively) till 500°C.

Table (4.13): The products composition as a function of temperature for 2-pentene reaction over WO_3/MCM-41

Yield (%)	Temperature (°C)						
	200	**250**	**300**	**350**	**400**	**450**	**500**
Conversion	6.400	8.100	10.000	12.700	20.000	35.800	67.900
Ethylene							1.400
Propylene					0.700	3.600	12.700
Butenes					2.000	8.700	22.100
C_5 Isomers	6.400	8.100	10.000	12.700	15.700	14.800	12.300
C_5 Feed	93.600	91.900	90.000	87.300	80.000	64.200	32.200
C_6^+					1.700	8.700	19.300
Aromatics							
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000

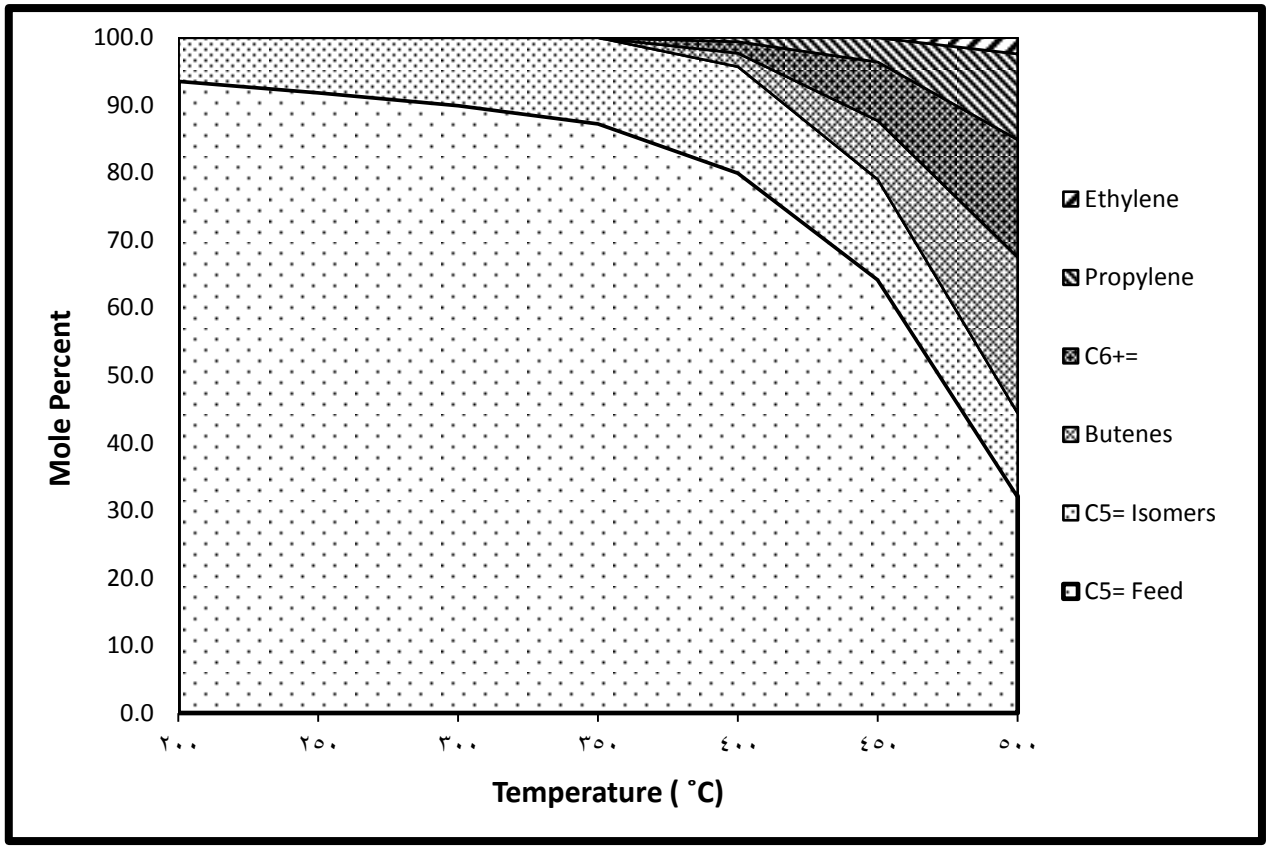


Figure (4.8): Variation in the products composition as a function of temperature for 2-pentene reaction over WO_3 /MCM-41.

In the case of WO_3 /SBA-15 $C_5^=$ isomerization products were observed from 200 to 400°C and metathesis products ethylene, propylene, butenes and $C_{6+}^=$ (0.0, 2.8, 7.3 & 8.2 % respectively) appeared in the product mixtures at 450°C and their amount further increased (1.1, 8.9, 18.3 & 18.8 % respectively) till 500°C.

Table (4.14): The products composition as a function of temperature for 2-pentene reaction over WO_3 /SBA-15

Yield (%)	Temperature (°C)						
	200	**250**	**300**	**350**	**400**	**450**	**500**
Conversion	1.800	4.800	7.100	9.900	13.400	30.600	56.500
Ethylene							1.100
Propylene						2.800	8.900
Butenes						7.300	18.300
C_5 Isomers	1.800	4.800	7.100	9.900	13.400	12.300	8.400
C_5 Feed	98.200	95.200	92.900	90.100	86.600	69.400	43.500
C_6^+						8.200	18.800
Aromatics							1.000
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000

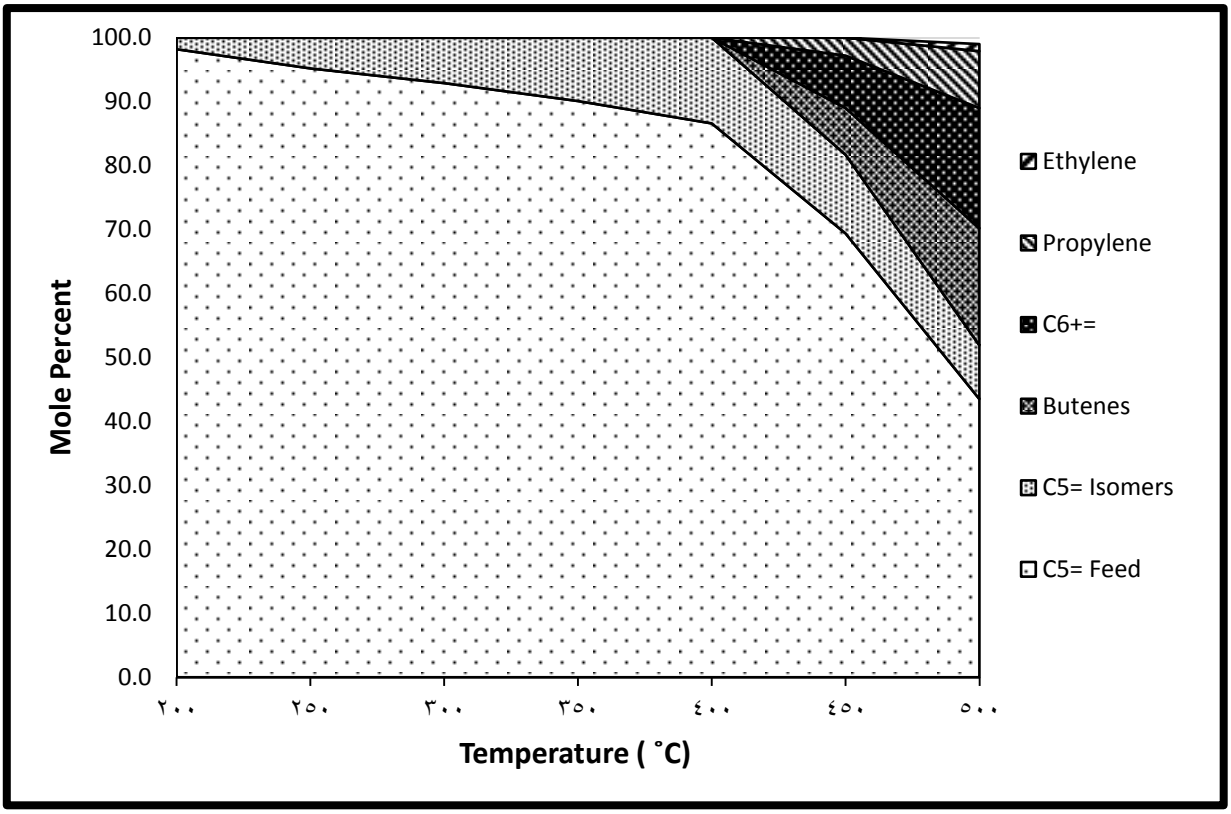


Figure (4.9): Variation in the products composition as a function of temperature for 2-pentene reaction over WO_3/SBA-15.

The changes in product distribution clearly indicated that Mo oxide supported catalysts exhibited metathesis activity at lower reaction temperatures than WO_3 supported catalysts, which is in accordance with literature data [12].

4.2.3 Catalyst Stability

Metathesis of 2-pentene over MoO_3 /MCM-22, $MoO_2(acac)_2$ /SBA-15, $MoO_2(acac)_2$ /MCM-41, WO_3 /SBA-15, and WO_3 /MCM-41 was carried out at 500˚C for 720 minutes to study the catalyst stability (Tables (4.15)-(4.19) and Figure (4.10)). It was observed that 2-pentene conversion over MCM-41 based catalysts (i.e. $MoO_2(acac)_2$ /MCM-41 and WO_3 /MCM-41) was quite stable. The 2-pentene conversion was only dropped from 50.0 to 48.5 over $MoO_2(acac)_2$ /MCM-41 and 67.9 to 66.5% over WO_3 /MCM-41 over 720 minutes.

Table (4.15): Stability test for WO_3 /MCM-41 catalyst at 500°C and atmospheric pressure.

Time (hour)	Conversion (%)
2	67.9
3	67.5
4	67.8
5	67.1
6	67.7
7	66.2
8	67.2
9	67.9
10	67.1
11	66.1
12	66.5

Table (4.16): Stability test for $MoO_2(acac)_2$ /MCM-41 catalyst at 500°C and atmospheric pressure.

Time (hour)	Conversion (%)
2	50.0
3	49.9
4	49.8
5	48.9
6	49.5
7	48.8
8	48.3
9	47.5
10	47.7
11	48.7
12	48.5

The catalysts based on SBA-15 (i.e. $MoO_2(acac)_2$ /SBA-15 and WO_3 /SBA-15) were less stable. The 2-pentene conversion was dropped from 41.5 to 34.6 % over $MoO_2(acac)_2$ / SBA-15 and 56.5 to 50.4 % over WO_3 /SBA-15 over 720 minutes.

Table (4.17): Stability test for WO_3 /SBA-15 catalyst at 500°C and atmospheric pressure.

Time (hour)	Conversion (%)
2	56.5
3	54.6
4	54.5
5	54.4
6	53.6
7	52.3
8	51.8
9	51.8
10	52.1
11	52.2
12	50.4

Table (4.18): Stability test for $MoO_2(acac)_2$ /SBA-15 catalyst at 500°C and atmospheric pressure.

Time (hour)	Conversion (%)
2	41.5
3	42.1
4	43.3
5	41.9
6	42.6
7	38.9
8	39.3
9	36.0
10	35.9
11	34.6
12	34.6

The highest drop in conversion was observed over MoO_3 /MCM-22 from 78.7 to 61.0 %. We have analyzed coke amount (in terms of total carbon amount) in two spent catalysts MoO_3 /MCM-22 and WO_3 /MCM-41. In the former case 101.73 mg C/g was found but in the latter case only 23.14 mg C/g. It evidences a higher extent of coke formation for MCM-22 based catalyst, which may result in a faster loss of its catalyst activity.

Table (4.19): Stability test for MoO_3 /MCM-22 catalyst at 500°C and atmospheric pressure.

Time (hour)	Conversion (%)
2	78.7
3	75.5
4	71.7
5	68.4
6	66.7
7	66.2
8	62.8
9	63.2
10	63.0
11	62.9
12	61.0

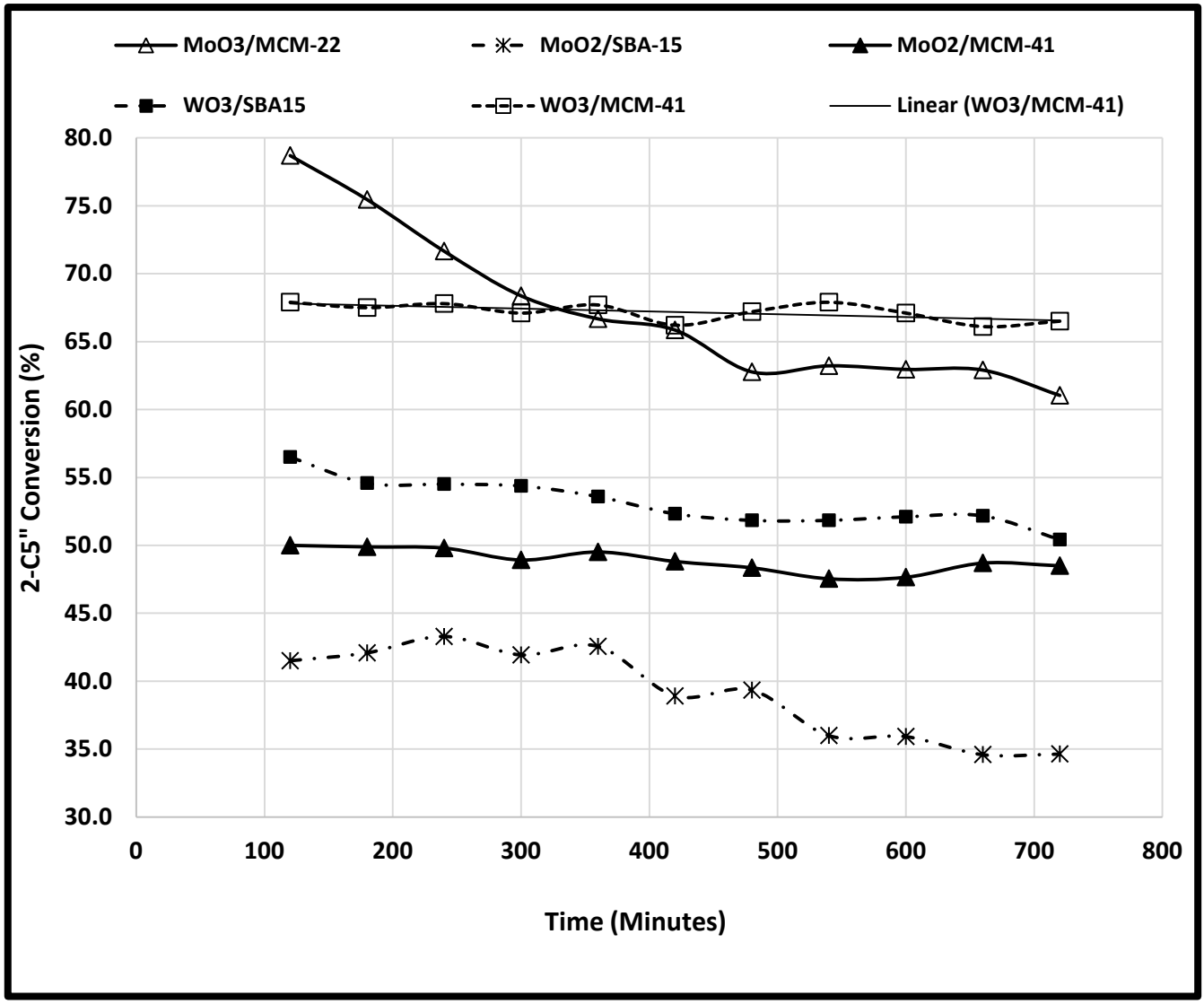
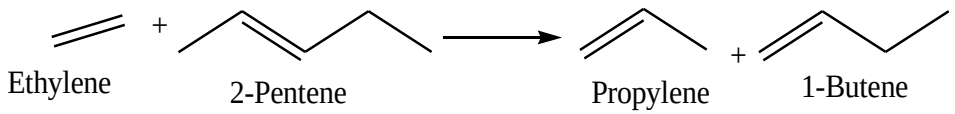


Figure (4.10): Conversion of 2-pentene as a function of time over different catalysts at 500°C and atmospheric pressure.

4.2.4 Effect of Addition of Ethylene as Feed with 2-Pentene

Metathesis reaction of ethylene with 2-pentene produces propylene and 1-butene as shown below in equation (4.1):



(4.1)

Therefore in order to investigate the effect of addition of ethylene on the metathesis reaction of 2-pentene over different catalysts the reaction temperature and GHSV were set at 500˚C and 1200h^{-1}. The molar ratio of 2-pentene to ethylene was set to 1:0 and 1:1 (Tables (4.20) - (4.24) and Figures (4.11) - (4.14)).

It was observed that selectivity to propylene was increased when ethylene was added to 2-pentene in molar ratio 1:1 over $MoO_2(acac)_2$ /SBA-15 (12.9 to 34.2 %), $MoO_2(acac)_2$ /MCM-41 (15.1 to 36.6 %), WO_3 /SBA-15 (15.7 to 40.3 %) and WO_3 / MCM-41 (18.7 to 47 %). It was also noted that there was a little increase in C_4 olefins due to ethylene addition (mainly 1-$C_4^=$ (Figure (4.14))) but there was drastic drop in selectivity of $C_{6+}^=$ species over $MoO_2(acac)_2$ /SBA-15 (24.0 to 7), $MoO_2(acac)_2$ /MCM-41 (30.1 to 8), WO_3 /SBA-15 (33.5 to 8) & WO_3 / MCM-41 (28.5 to 5 %). These observations clearly indicate that all these catalysts are performing metathesis reactions. Therefore when feed is 2-C_5 (alone) the C_4 olefins and C_6^+ olefins are the major products. However when ethylene is added in the feed then major reaction is metathesis reaction between ethylene and 2-C_5 resulting in production of propylene and C_4 olefin as the major products. Also presence of small amount of $C_{6+}^=$ indicated that self-metathesis of 2-pentene also took place.

It was noted that tungsten based catalysts i.e. WO_3 /SBA-15 & WO_3 /MCM-41 exhibited higher conversion of 2-$C_5^=$ (56.5 & 67.9 % respectively) and higher selectivity to propylene (40.3 & 47.0 % respectively) as compared to those of molybdenum based catalysts both in metathesis of 2-pentene alone or cross metathesis of 2-pentene and ethylene. The selectivity to propylene increased in the order $MoO_2(acac)_2$ /SBA-15 < $MoO_2(acac)_2$ /MCM-41 < WO_3 /SBA-15 < WO_3 /MCM-41.

Table (4.20): Selectivity (mole %) of products during metathesis reaction of 2-pentene with ethylene at 500°C over $MoO_2(acac)_2$ /SBA-15

Selectivity (mole %)	**$MoO_2(acac)_2$ /SBA-15**	
2-$C_5^=$:$C_2^=$ Ratio	1:0	1:1
Conversion of 2-$C_5^=$	41.5	42.3
Conversion of $C_2^=$	0	18.6
C_1	0	0
C_2	0	0
$C_2^=$	1.9	0
C_3	0	0
$C_3^=$	12.5	34.2
i-C_4	0	0
n-C_4	0	0
1-$C_4^=$	8.7	16.1
t-2-$C_4^=$	10.3	9.8
i-$C_4^=$	0	0
c-2-$C_4^=$	7.7	7.5
i-C_5	0	0
n-C_5	0	0
3-Me-1-$C_4^=$	0	0
1-$C_5^=$	27.4	22.3
2-Me-2-$C_4^=$	7.5	3.0
$C_{6+}^=$	24.0	7.1
Aromatics	0	0

Table (4.21): Selectivity (mole %) of products during metathesis reaction of 2-pentene with ethylene at 500°C over $MoO_2(acac)_2$ /MCM-41

Selectivity (mole %)	**$MoO_2(acac)_2$ /MCM-41**	
2-$C_5^=$:$C_2^=$ Ratio	1:0	1:1
Conversion of 2-$C_5^=$	50.0	51.0
Conversion of $C_2^=$	0	20.4
C_1	0.6	0
C_2	0	0
$C_2^=$	2.0	0
C_3	0	0
$C_3^=$	15.2	36.6
i-C_4	0	0
n-C_4	0	0
1-$C_4^=$	9.4	14.8
t-2-$C_4^=$	12.0	11.0
i-$C_4^=$	0	0
c-2-$C_4^=$	8.6	8.4
i-C_5	0	0
n-C_5	0.8	0
3-Me-1-$C_4^=$	0	0
1-$C_5^=$	17.8	17.8
2-Me-2-$C_4^=$	3.2	3.1
$C_{6+}^=$	30.1	8.4
Aromatics	0.4	0

Table (4.22): Selectivity (mole %) of products during metathesis reaction of 2-pentene with ethylene at 500°C over WO_3 /SBA-15

Selectivity (mole %)	**WO_3 /SBA-15**	
2-$C_5^=$:$C_2^=$ Ratio	1:0	1:1
Conversion of 2-$C_5^=$	56.5	57.2
Conversion of $C_2^=$	0	28.0
C_1	0	0
C_2	0	0
$C_2^=$	2.0	0
C_3	0	0
$C_3^=$	15.8	40.3
i-C_4	0	0
n-C_4	0	0
1-$C_4^=$	9.9	18.6
t-2-$C_4^=$	12.2	10.9
i-$C_4^=$	1.4	0
c-2-$C_4^=$	9.0	8.0
i-C_5	0	0
n-C_5	0	0
3-Me-1-$C_4^=$	0	0
1-$C_5^=$	10.3	11.4
2-Me-2-$C_4^=$	4.6	3.3
$C_{6+}^=$	33.5	7.5
Aromatics	1.2	0

Table (4.23): Selectivity (mole %) of products during metathesis reaction of 2-pentene with ethylene at 500°C over WO_3/MCM-41

Selectivity (mole %)	**WO_3/MCM-41**	
2-$C_5^=$:$C_2^=$ Ratio	1:0	1:1
Conversion of 2-$C_5^=$	67.9	68.5
Conversion of $C_2^=$	0	49.6
C_1	0	0
C_2	0	0
$C_2^=$	2.1	0
C_3	0	0
$C_3^=$	18.7	47.0
i-C_4	0	0
n-C_4	0	0
1-$C_4^=$	9.1	12.5
t-2-$C_4^=$	12.7	13.6
i-$C_4^=$	1.3	1.7
c-2-$C_4^=$	9.4	10.3
i-C_5	0	0
n-C_5	0	0
3-Me-1-$C_4^=$	0	0
1-$C_5^=$	8.5	5.1
2-Me-2-$C_4^=$	9.7	4.6
$C_{6+}^=$	28.4	5.2
Aromatics	0	0

In the case of MoO_3 /MCM-22 there was a little increase in propylene selectivity from 18.7 to 24.5 % (1:1 ratio) after ethylene addition and also selectivity of 2-methyl-2-butene was increased from 26.6 to 33.4% (1:1 ratio) due to skeletal isomerization (Figure (4.13)). On the other hand, there was a little drop in selectivity of $C_{6+}^{=}$ (8.1 to 4.7 %). The product selectivity was almost the same using 2-pentene only or a mixture of ethylene and 2-pentene.

This observation clearly indicates that MoO_3/MCM-22 is not conducting metathesis reactions probably and causes cracking as the major reaction under these conditions.

Table (4.24): Selectivity (mole %) of products during metathesis reaction of 2-pentene with ethylene at 500°C over MoO_3 /MCM-22

Selectivity (mole %)	**MoO_3 /MCM-22**	
2-$C_5^=$: $C_2^=$ Ratio	1:0	1:1
Conversion of 2-$C_5^=$	78.7	77.9
Conversion of $C_2^=$	0	5.6
C_1	0	0
C_2	0	0.6
$C_2^=$	8.5	0
C_3	1.8	1.3
$C_3^=$	18.7	24.5
i-C_4	1.5	1.0
n-C_4	1.0	0
1-$C_4^=$	3.2	3.9
t-2-$C_4^=$	5.3	5.6
i-$C_4^=$	10.3	10.8
c-2-$C_4^=$	3.6	4.3
i-C_5	1.9	0
n-C_5	3.2	2.0
3-Me-1-$C_4^=$	2.2	3.1
1-$C_5^=$	2.9	4.7
2-Me-2-$C_4^=$	26.6	33.4
$C_{6+}^=$	8.0	4.7
Aromatics	1.3	0

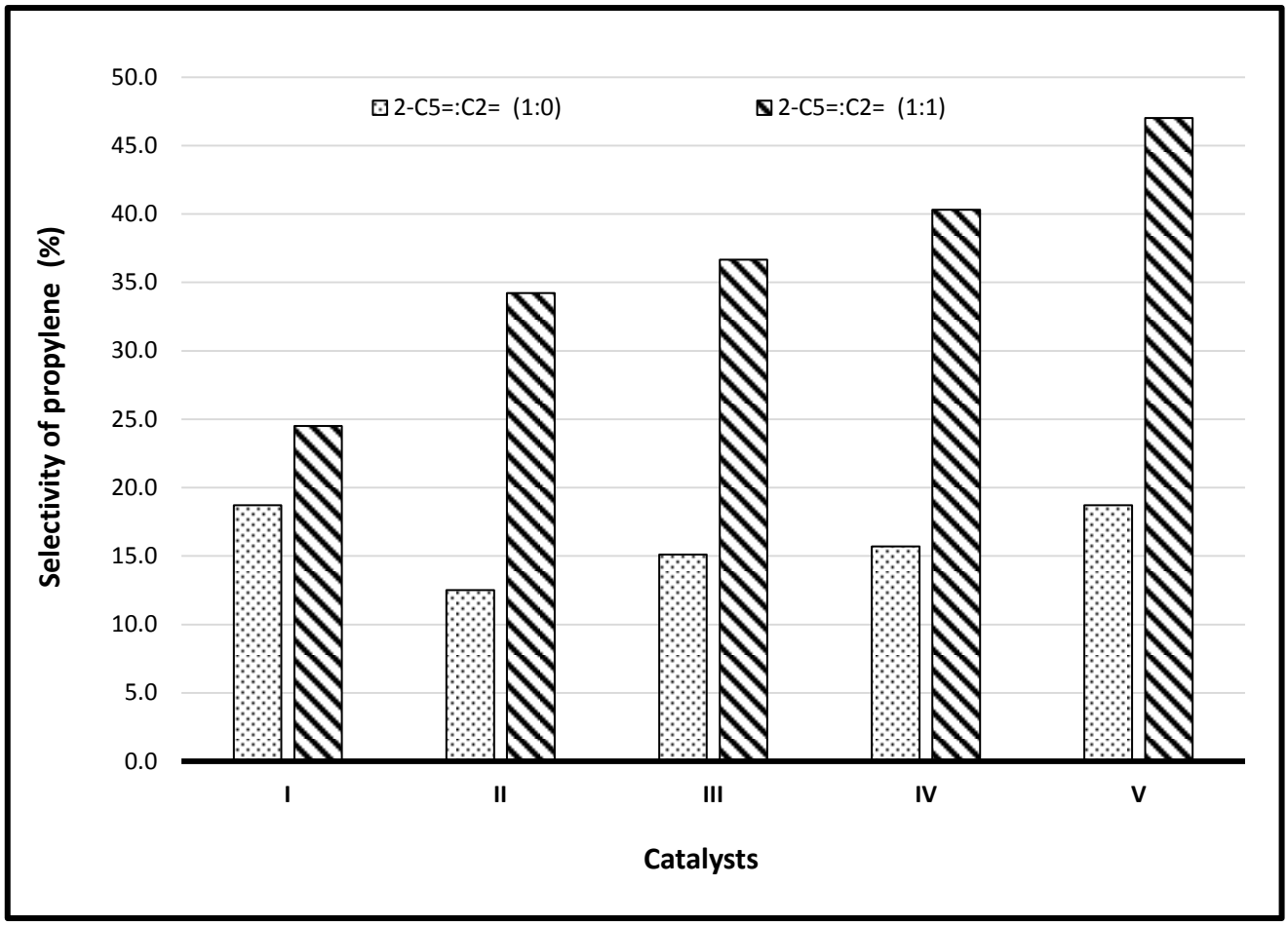


Figure (4.11): Selectivity of propylene over different catalysts under different ratios of 2-pentene: ethylene at 500°C and 1 atmospheric pressure.

Where:

(I) MoO_3 /MCM-22

(II) $MoO_2(acac)_2$ /SBA-15

(III) $MoO_2(acac)_2$ /MCM-41

(IV) WO_3 /SBA-15

(V) WO_3 /MCM-41

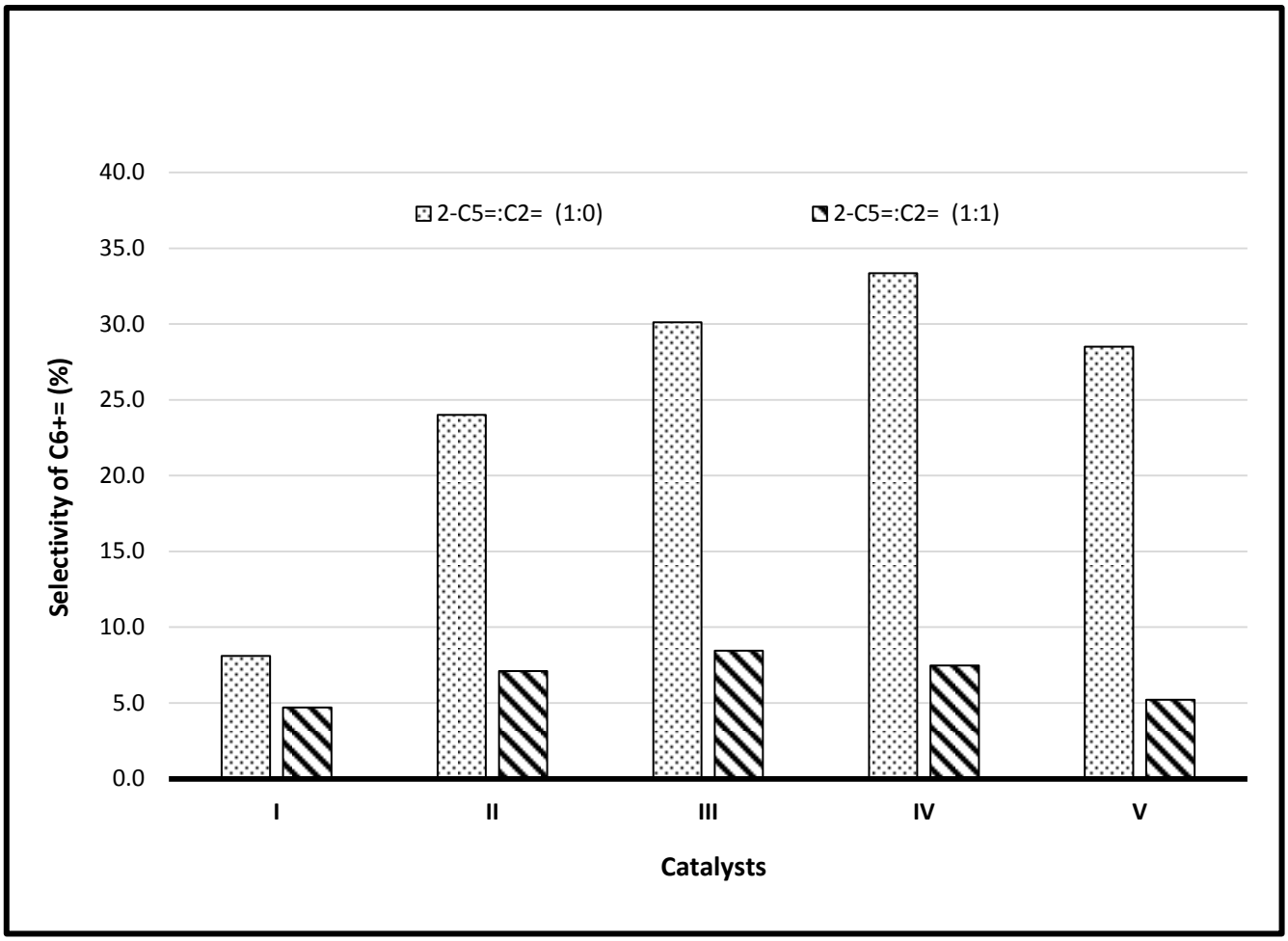


Figure (4.12): Selectivity of $C_{6+}^{=}$ over different catalysts under different ratios of 2-pentene: ethylene at 500°C and 1 atmospheric pressure.

Where:

(I) MoO_3 /MCM-22

(II) $MoO_2(acac)_2$ /SBA-15

(III) $MoO_2(acac)_2$ /MCM-41

(IV) WO_3 /SBA-15

(V) WO_3 /MCM-41

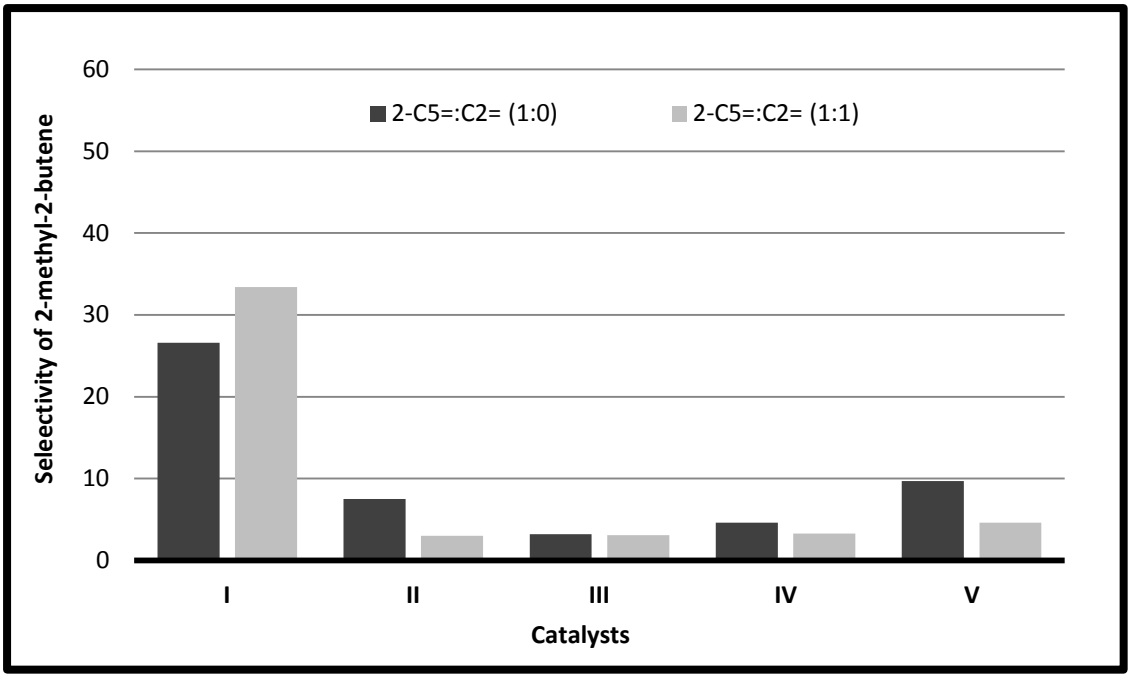


Figure (4.13): Selectivity of 2-methyl-2-butene over different catalysts under different ratios of 2-pentene: ethylene at 500°C and 1 atmospheric pressure.

Where:

(I) MoO_3 /MCM-22

(II) $MoO_2(acac)_2$ /SBA-15

(III) $MoO_2(acac)_2$ /MCM-41

(IV) WO_3 /SBA-15

(V) WO_3 /MCM-41

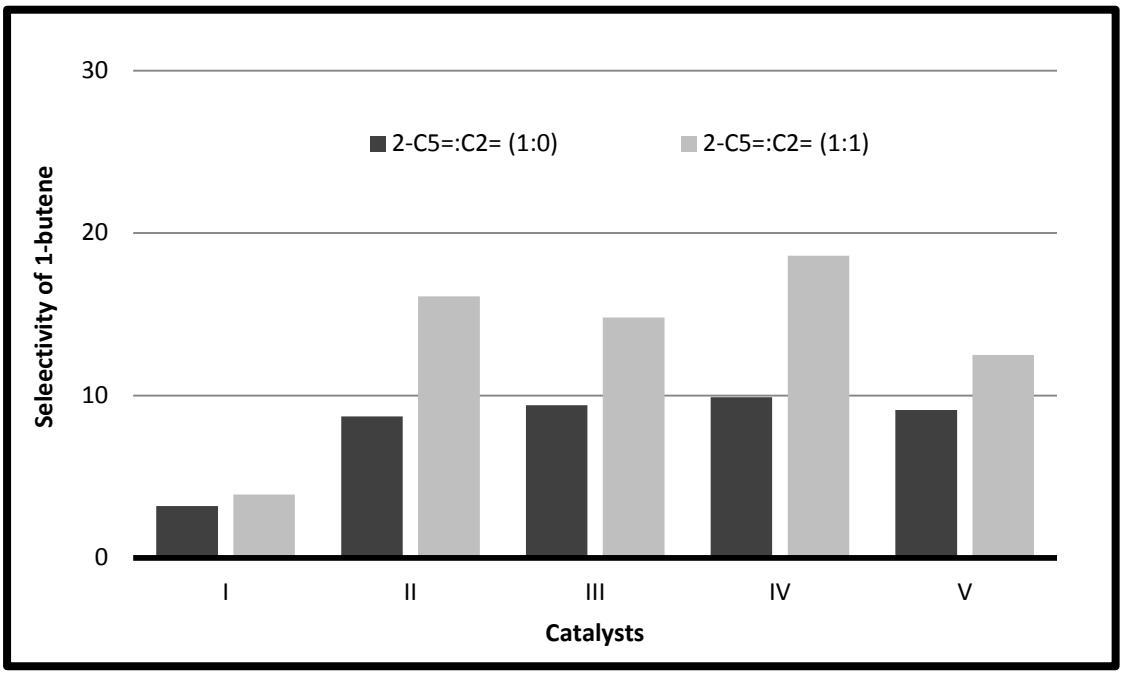


Figure (4.14): Selectivity of 1-butene over different catalysts under different ratios of 2-pentene: ethylene at 500°C and 1 atmospheric pressure.

Where:

(I) MoO_3 /MCM-22

(II) $MoO_2(acac)_2$ /SBA-15

(III) $MoO_2(acac)_2$ /MCM-41

(IV) WO_3 /SBA-15

(V) WO_3 /MCM-41

4.2.5 Effect of Catalyst Amount (0.5 ml & 1 ml)

We have evaluated four catalysts ($MoO_2(acac)_2$ /MCM-41, $MoO_2(acac)_2$ /SBA-15, MoO_3 /SBA-15 and WO_3 /SBA-15) for metathesis reaction at 500ºC and atmospheric pressure with amount of catalyst as 0.5 ml and 1.0 ml in order to investigate the effect of increasing the catalyst amount on conversion and product distribution.

It was observed that increasing the catalyst loading from 0.5 ml to 1 ml resulted in increase of propylene yield and conversion due to increasing in contact time between the reactants and catalyst bed (GHSV decreased from 1200 hr^{-1} to 600 hr^{-1})

$MoO_2(acac)_2$ /MCM-41 exhibited 66.7 % and 50% conversion respectively over 1.0 & 0.5 ml of catalyst and propylene yield increased from 7.6 to 10%. Catalysts WO_3 /SBA-15 exhibited the highest activity with 80 % conversion for 1.0 ml of catalyst and 56.5 % with 0.5 ml of catalyst with high increase of propylene yield from 8.9 to 16.9%. $MoO_2(acac)_2$ /SBA-15 exhibited 53.22 % and 41.541% conversion respectively over 1.0 & 0.5 ml of catalyst and propylene yield increased from 5.2 to 7.3%. MoO_3 /SBA-15 exhibited the lowest activity with 39.1% conversion for 1.0 ml of catalyst and 46.4 % with 0.5 ml of catalyst with very slight increase of propylene yield from 5 to 5.5%.

Table (4.25): Product distribution over $MoO_2(acac)_2$ /MCM-41under different catalyst loading at 500°C and 1 atmospheric pressure

Component name	Yield (mol %)	
	Catalyst 0.5 ml	Catalyst 1 ml
2-$C_5^=$ Conversion	50.0	66.7
C_1	0.3	0.3
C_2	0.0	0.2
$C_2^=$	1.0	2.9
C_3	0.0	0.2
$C_3^=$	7.6	10.0
i-C_4	0.0	0.0
n-C_4	0.0	0.0
1-$C_4^=$	4.7	5.5
t-2-$C_4^=$	6.0	7.7
i-$C_4^=$	0.0	0.4
c-2-$C_4^=$	4.3	5.7
i-C_5	0.0	0.0
n-C_5	0.4	0.4
3-Me-1-$C_4^=$	0.0	0.3
1-$C_5^=$	9.0	7.0
t-2-$C_5^=$	32.4	20.5
c-2-$C_5^=$	17.5	12.8
2-Me-2-$C_4^=$	1.6	3.7
$C_6^=$	8.8	12.9
$C_7^=$	4.4	6.3
$C_8^=$	1.6	2.3
$C_9^=$+	0.3	0.5
Aromatics	0.2	0.4

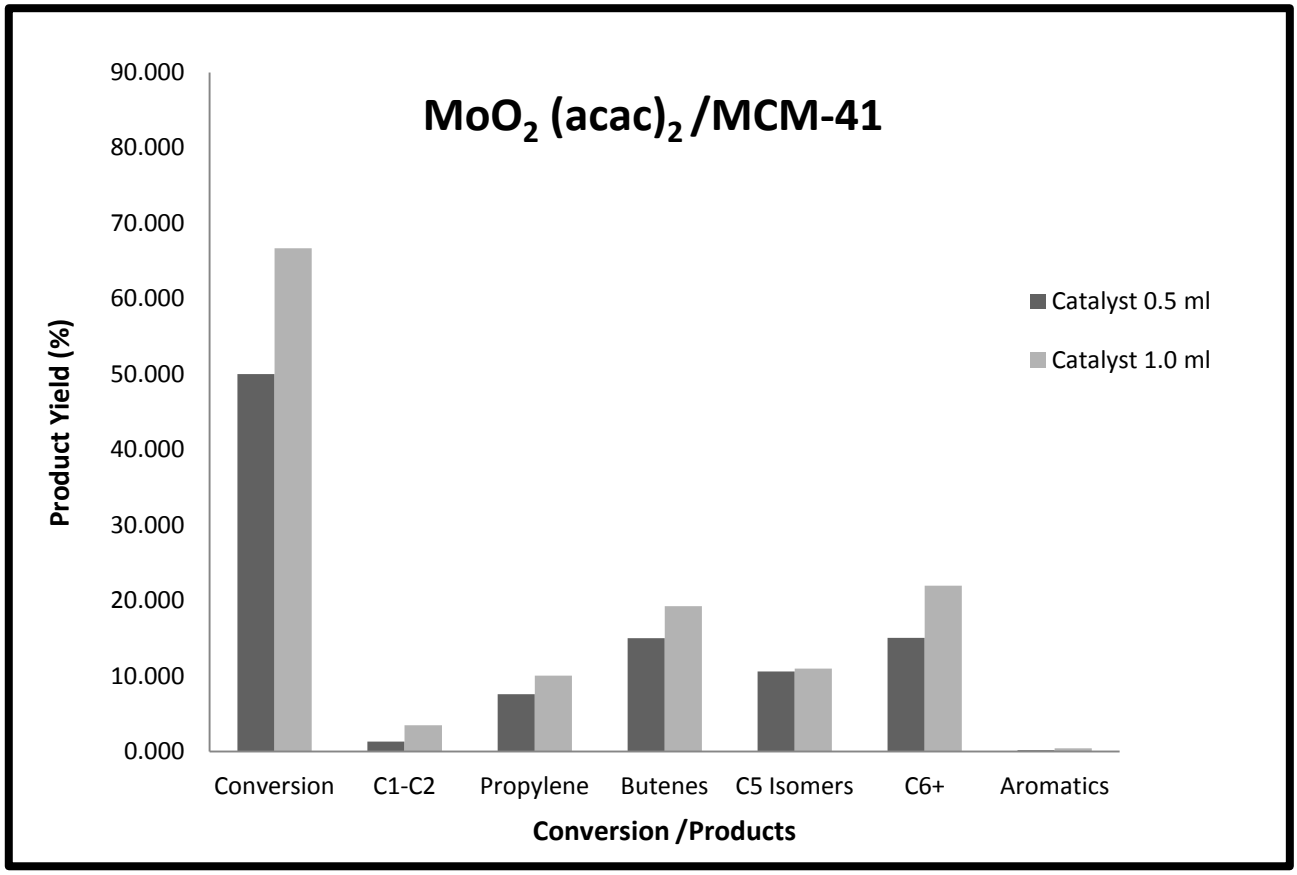


Figure (4.15): Comparison of performance of $MoO_2(acac)_2$ /MCM-41under different catalyst loading at 500°C and 1 atmospheric pressure

Table (4.26): Product distribution over WO_3 /SBA-15 under different catalyst loading at 500°C and 1 atmospheric pressure

Component name	Yield (mol %)	
	Catalyst 0.5 ml	Catalyst 1 ml
2-$C_5^=$ Conversion	56.5	80.2
C_1	0.0	0.0
C_2	0.0	0.0
$C_2^=$	1.1	2.4
C_3	0.0	0.0
$C_3^=$	8.9	16.9
i-C_4	0.0	0.0
n-C_4	0.0	0.0
1-$C_4^=$	5.6	7.7
t-2-$C_4^=$	6.9	12.5
i-$C_4^=$	0.8	0.0
c-2-$C_4^=$	5.1	8.2
i-C_5	0.0	0.0
n-C_5	0.0	0.0
3-Me-1-$C_4^=$	0.0	0.0
1-$C_5^=$	5.8	3.5
t-2-$C_5^=$	27.8	11.9
c-2-$C_5^=$	15.8	7.9
2-Me-2-$C_4^=$	2.6	2.8
$C_6^=$	11.6	14.0
$C_7^=$	5.0	7.1
$C_8^=$	1.8	3.5
$C_9^=$+	0.5	1.1
Aromatics	1.0	0.6

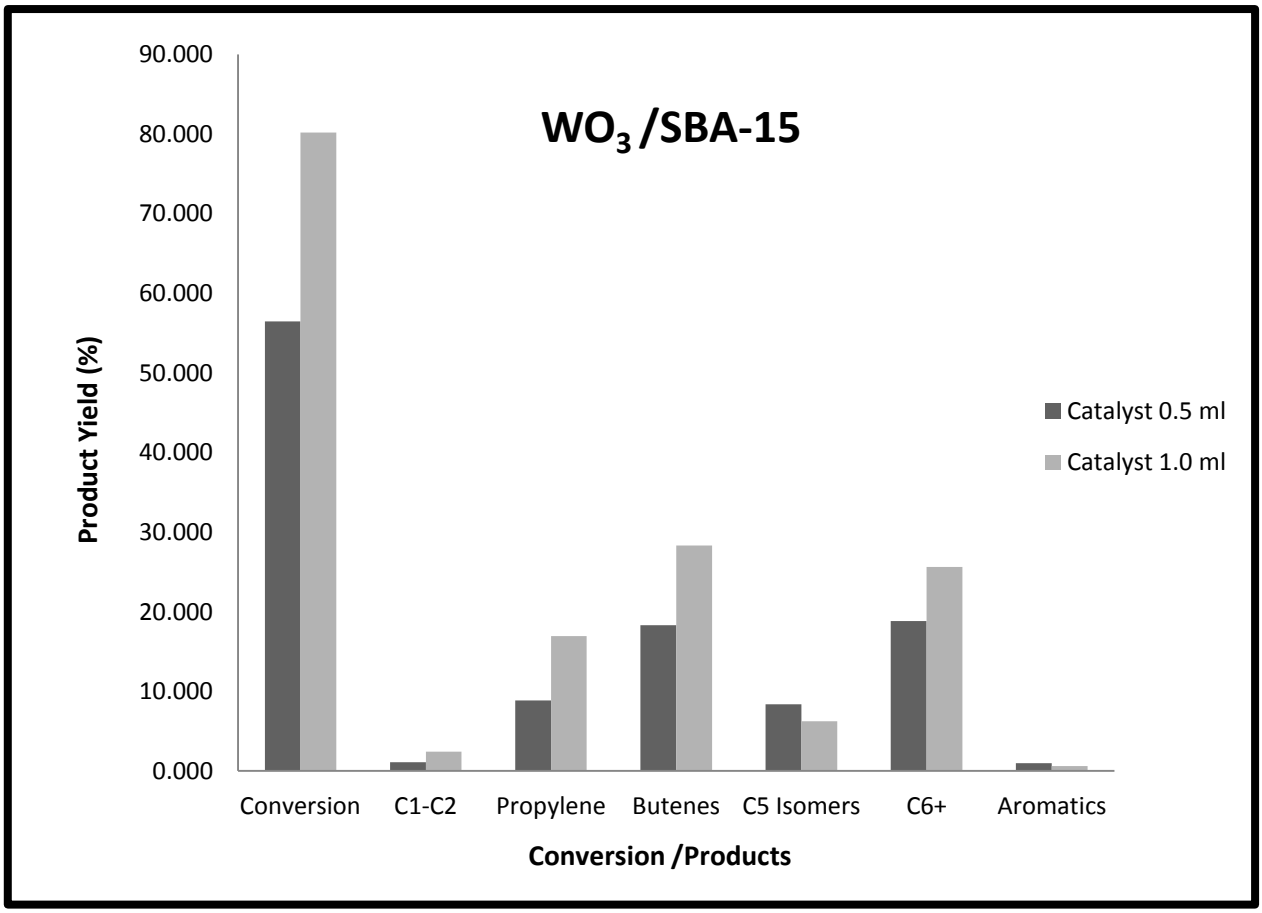


Figure (4.16): Comparison of performance of WO_3 /SBA-15 under different catalyst loading at 500°C and 1 atmospheric pressure

Table (4.27): Product distribution over $MoO_2(acac)_2$ /SBA-15 under different catalyst loading at 500°C and 1 atm

Component name	Yield (mol %)	
	Catalyst 0.5 ml	Catalyst 1 ml
2-$C_5^=$ Conversion	41.5	53.2
C_1	0.0	0.0
C_2	0.0	0.0
$C_2^=$	0.8	0.9
C_3	0.0	0.0
$C_3^=$	5.2	7.3
i-C_4	0.0	0.0
n-C_4	0.0	0.0
1-$C_4^=$	3.6	5.1
t-2-$C_4^=$	4.3	6.5
i-$C_4^=$	0.0	0.0
c-2-$C_4^=$	3.2	4.8
i-C_5	0.0	0.0
n-C_5	0.0	0.5
3-Me-1-$C_4^=$	0.0	0.0
1-$C_5^=$	11.4	8.9
t-2-$C_5^=$	37.2	30.0
c-2-$C_5^=$	21.2	16.8
2-Me-2-$C_4^=$	3.1	2.2
$C_6^=$	7.1	10.9
$C_7^=$	2.6	4.7
$C_8^=$	0.3	1.5
$C_9^=$+	0.0	0.0
Aromatics	0.0	0.0

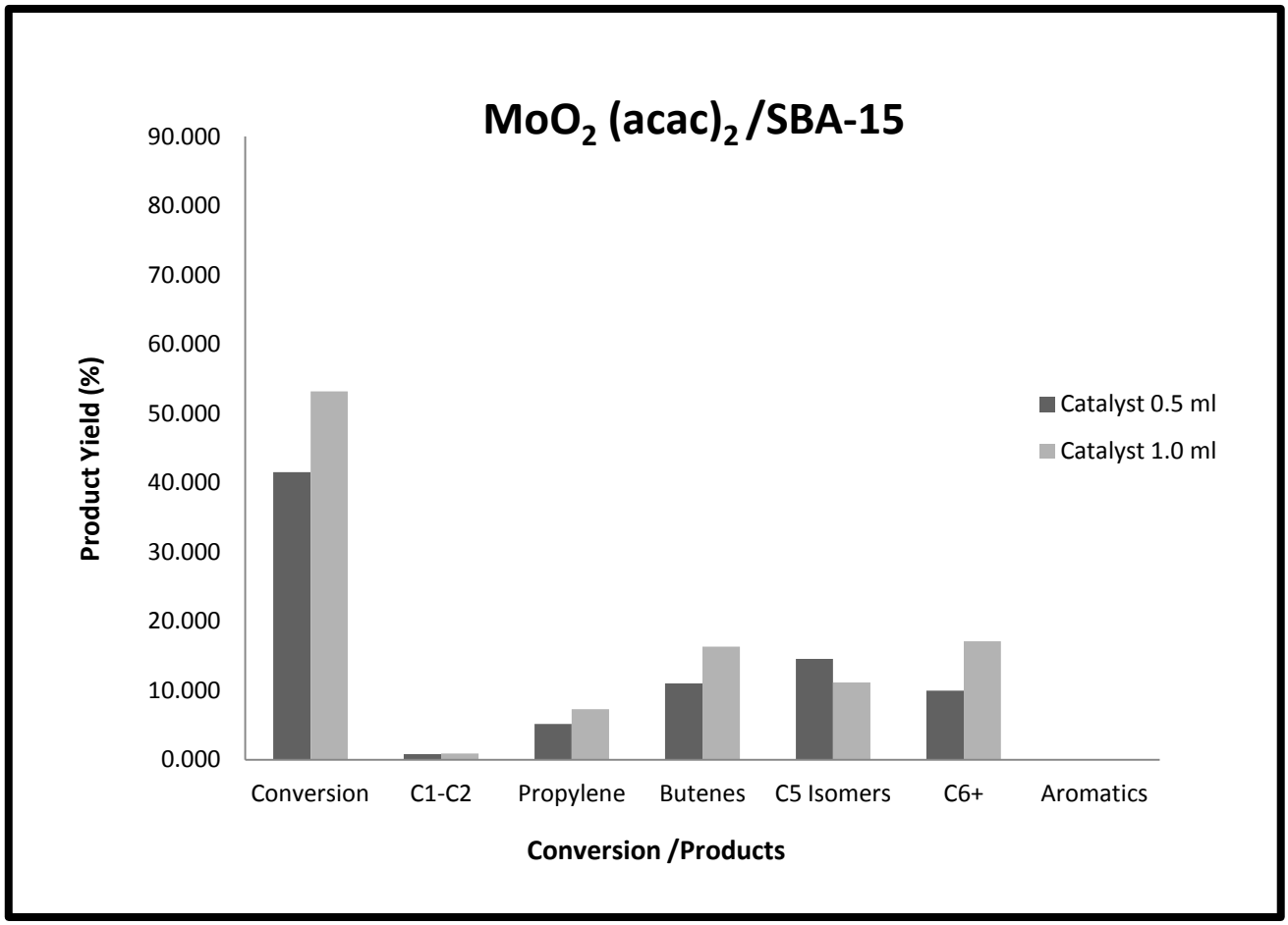


Figure (4.17): Comparison of performance of $MoO_2(acac)_2$ /SBA-15 under different catalyst loading at 500°C and 1 atmospheric pressure

Table (4.28): Product distribution over MoO_3/SBA-15 under different catalyst loading at 500°C and 1 atm

Component name	Yield (mol %)	
	Catalyst 0.5 ml	Catalyst 1 ml
2-$C_5^=$ Conversion	39.1	46.4
C_1	0.5	0.0
C_2	0.0	0.0
$C_2^=$	0.8	0.8
C_3	0.0	0.0
$C_3^=$	5	5.5
i-C_4	0.0	0.0
n-C_4	0.0	0.0
1-$C_4^=$	3.8	3.8
t-2-$C_4^=$	4.5	4.8
i-$C_4^=$	0.0	0.0
c-2-$C_4^=$	3.2	3.53
i-C_5	0.0	0.0
n-C_5	0.3	0.35
3-Me-1-$C_4^=$	0.0	0.0
1-$C_5^=$	9.2	10.3
t-2-$C_5^=$	40.1	34.3
c-2-$C_5^=$	20.8	19.3
2-Me-2-$C_4^=$	1.7	2.5
$C_6^=$	6.4	8.6
$C_7^=$	2.5	3.8
$C_8^=$	0.8	1.6
$C_9^=$+	0	0.5
Aromatics	0.3	0.3

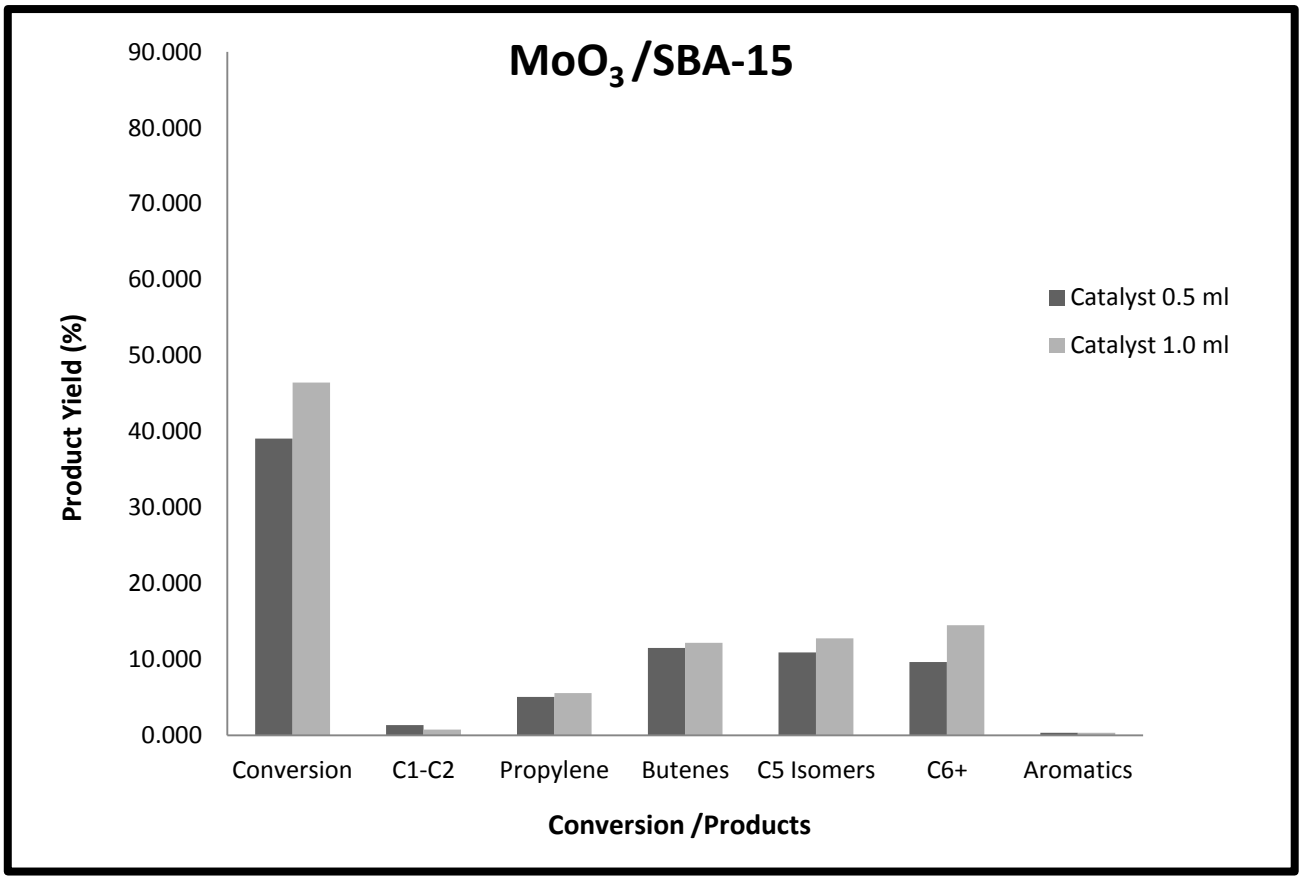


Figure (4.18): Comparison of performance of MoO_3 /SBA-15 under different catalyst loading at 500°C and 1 atmospheric pressure.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

2-pentene can be effectively transformed to propylene, butenes and $C_{6+}^{=}$ over Mo and W oxides catalysts under conditions suitable for industrial applications. The activity and selectivity of mentioned catalysts were found to depend strongly on used supports.

The results of the thesis work can be summarized as below:

1. Catalysts having molybdenum and tungsten oxides supported on mesoporous molecular sieves (MCM-41 and SBA-15) exhibited metathesis of 2-pentene as a strongly prevailing reaction. Catalysts based on MCM-41 exhibited higher activity and stability as compared to that of SBA-15.

2. Catalysts having molybdenum oxide supported on conventional silica exhibited only 2-pentene isomerization in low conversions.

3. Catalysts having molybdenum oxide supported on MCM-22 exhibited mainly isomerization and cracking reactions at the highest 2 pentene conversions.

4. Addition of ethylene in the feed resulted into increased selectivity of propylene due to cross metathesis reaction between ethylene and 2-pentene.

5. Increasing of reaction temperature (from 200 to 500 ºC) resulted into increased the yield of all products and conversion of C_5 olefins.

6. Catalyst based on MCM-41 is a better choice from industrial point of view due to its higher activity and lower cost of support (due to the cheaper structure directing agent) as compared to SBA-15 based catalysts.

7. Increasing the catalyst loading from 0.5 ml to 1 ml resulted in increase of propylene yield and conversion due to increasing in contact time between the reactants and catalyst bed**.**

5.2 Recommendations:

Regarding all these results and studies that showed the ability of WO_3 and MoO_2 supported on MCM-22, SBA-15 and MCM-41 catalyst for the 2-pentene metathesis to propylene, the following recommendations can be advanced for future studies:

1. A Comperhensive study of isomerization and cracking reactions that happen as a side reaction of 2-pentene metathesis should be conducted.

2. Catalysts with two or more metals with different loading supported on mesoporous materials should be tested to get higher conversion and propylene yield.

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